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

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

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1 The pseudo-Jahn-Teller stabilization energy of LS [Co(tpy)_2]^2+

Table 1 gives the calculated values of the PJT stabilization energy $E_{\text{PJT}}$ defined as the electronic energy difference:

$$E_{\text{PJT}} = E^{\text{el}}(2\text{B}_2) - E^{\text{el}}(2\text{A}_1).$$

Nearly identical $E_{\text{PJT}}$ values are obtained with the $\mathcal{S}$ and $\mathcal{G}$ 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 $E_{\text{PJT}}$. All functionals indeed consistently predict that $E_{\text{PJT}}$ is small, with calculated values in the quite narrow 140~240 cm$^{-1}$ range. The standard deviation over the calculated $E_{\text{PJT}}$ values is $\sigma \approx 35$ cm$^{-1}$. Using an uncertainty of $2\sigma$ 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 $E_{\text{PJT}} = 205(70)$ cm$^{-1}$.

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

<table>
<thead>
<tr>
<th>Functional</th>
<th>$E_{\text{PJT}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/$\mathcal{G}$</td>
<td>137</td>
</tr>
<tr>
<td>B3LYP*$\mathcal{G}$</td>
<td>174</td>
</tr>
<tr>
<td>HCTH407/$\mathcal{G}$</td>
<td>206</td>
</tr>
<tr>
<td>OLYP/$\mathcal{G}$</td>
<td>213</td>
</tr>
<tr>
<td>OLYP/$\mathcal{S}$</td>
<td>232</td>
</tr>
<tr>
<td>OPBE/$\mathcal{S}$</td>
<td>213</td>
</tr>
<tr>
<td>OPBE/$\mathcal{G}$</td>
<td>210</td>
</tr>
<tr>
<td>RPBE/$\mathcal{S}$</td>
<td>218</td>
</tr>
<tr>
<td>BLYP/$\mathcal{S}$</td>
<td>234</td>
</tr>
<tr>
<td>PBE/$\mathcal{G}$</td>
<td>237</td>
</tr>
<tr>
<td>PBE/$\mathcal{S}$</td>
<td>241</td>
</tr>
</tbody>
</table>

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 $\Delta_{\text{HS}}$ defined by the electronic energy difference:

$$\Delta_{\text{HS}} = E^{\text{el}}(4\text{E}) - E^{\text{el}}(4\text{A}_2).$$

Table 2 Calculated values of the tetragonal splitting of the HS state, $\Delta_{\text{HS}}$, in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Functional</th>
<th>$\Delta_{\text{HS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLYP/$\mathcal{S}$</td>
<td>+423</td>
</tr>
<tr>
<td>OLYP/$\mathcal{S}$</td>
<td>+565</td>
</tr>
<tr>
<td>OLYP/$\mathcal{S}$</td>
<td>+702</td>
</tr>
<tr>
<td>OPBE/$\mathcal{S}$</td>
<td>+456</td>
</tr>
<tr>
<td>PBE/$\mathcal{S}$</td>
<td>+557</td>
</tr>
</tbody>
</table>

These values are all positive, i.e., the $4\text{A}_2$ 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 $\approx 110 \text{ cm}^{-1}$ falls within the chemical accuracy of $350 \text{ cm}^{-1}$. This allows us to propose for $\Delta_{HS}$ a reliable estimate of $\Delta_{HS} = +540(110) \text{ cm}^{-1}$. 
3 Optimized geometries of \([\text{Co(tpy)}_2]^{2+}\) in the LS and in the HS state

Table 3 Bond lengths (Å) and angles (deg) in the optimized LS \(^2\text{B}_2\) \([\text{Co(tpy)}_2]^{2+}\) 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.

<table>
<thead>
<tr>
<th>Bond/Rotation Parameter</th>
<th>Exp. 1</th>
<th>ADF</th>
<th>G03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N′, Co-N′′</td>
<td>2.083</td>
<td>2.116(8)</td>
<td>2.115(22)</td>
</tr>
<tr>
<td>Co-N′′</td>
<td>1.912</td>
<td>1.892(8)</td>
<td>1.895(19)</td>
</tr>
<tr>
<td>N-C_2, N′′-C_2′</td>
<td>1.354</td>
<td>1.361(6)</td>
<td>1.357(4)</td>
</tr>
<tr>
<td>N-C_6, N′-C_6′</td>
<td>1.349</td>
<td>1.344(5)</td>
<td>1.339(4)</td>
</tr>
<tr>
<td>C_2-C_3, C_2′-C_3′</td>
<td>1.376</td>
<td>1.400(4)</td>
<td>1.396(3)</td>
</tr>
<tr>
<td>C_3-C_4, C_3′′-C_4′′</td>
<td>1.378</td>
<td>1.394(4)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C_4-C_5, C_4′-C_5′</td>
<td>1.384</td>
<td>1.395(4)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C_5-C_6, C_5′-C_6′′</td>
<td>1.384</td>
<td>1.395(4)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C_2′-C_2, C_6′-C_2′′</td>
<td>1.480</td>
<td>1.473(5)</td>
<td>1.472(5)</td>
</tr>
<tr>
<td>N′-C_2′, N′-C_6′′</td>
<td>1.350</td>
<td>1.363(6)</td>
<td>1.357(6)</td>
</tr>
<tr>
<td>C_2′-C_3′, C_2′-C_3′′</td>
<td>1.382</td>
<td>1.399(4)</td>
<td>1.396(3)</td>
</tr>
<tr>
<td>C_3′-C_4′, C_4′-C_3′′</td>
<td>1.379</td>
<td>1.394(4)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>(\alpha = \angle(C_6′′-C_2′′-C_2-C_2′))</td>
<td>106.5</td>
<td>107.5(2)</td>
<td>107.5(6)</td>
</tr>
<tr>
<td>(\beta = \angle(N′-\text{Co}-N) = \angle(N′′-\text{Co-N′}))</td>
<td>79.4</td>
<td>80.1(1)</td>
<td>80.0(3)</td>
</tr>
<tr>
<td>(\beta′ = \angle(N′′-\text{Co-N′}))</td>
<td>158.9</td>
<td>160.2(2)</td>
<td>160.0(6)</td>
</tr>
<tr>
<td>(\gamma = \angle(N′-C_2′-C_2-N) = \angle(N′′-C_2′′-C_6′-N′′))</td>
<td>1.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\eta = d(\text{Co-N′/Co-N′′}))</td>
<td>0.918</td>
<td>0.894(1)</td>
<td>0.896(4)</td>
</tr>
</tbody>
</table>

1 Data are for the \([\text{Co(tpy)}_2]^{2+}\) geometry of approximate \(D_{2d}\) symmetry found in the 120 K X-ray structure of LS \([\text{Co(tpy)}_2]I_2\cdot2\text{H}_2\text{O}\). 2 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 $^2\Lambda_1 [\text{Co(tpy)}]^{2+}$ 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.

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<thead>
<tr>
<th>Values of the selected structural parameters in the optimized LS geometries of C$_{2v}$ symmetry</th>
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</thead>
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<tr>
<td>Co-N, Co-N&quot;</td>
</tr>
<tr>
<td>Co-N&quot;</td>
</tr>
<tr>
<td>N-C$_2$, N&quot;-C$_2'$</td>
</tr>
<tr>
<td>N-C$_5$, N&quot;-C$_5'$</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_2'$-C$_2''$</td>
</tr>
<tr>
<td>C$_1$-C$_4$, C$_1'$-C$_1''$</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C$_4'$-C$_4''$</td>
</tr>
<tr>
<td>C$_3$-C$_6$, C$_3'$-C$_3''$</td>
</tr>
<tr>
<td>C$_2$-C$_5$, C$_2'$-C$_2''$</td>
</tr>
<tr>
<td>N&quot;-C$_2$, N&quot;-C$_5'$</td>
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<tr>
<td>C$_2$-C$_3$, C$_2'$-C$_2''$</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C$_3'$-C$_3''$</td>
</tr>
</tbody>
</table>

Structural changes upon the D$_{2d}$ → C$_{2v}$ symmetry lowering

<table>
<thead>
<tr>
<th>Structural parameters</th>
<th>ADF</th>
<th>L$_1$</th>
<th>L$_2$</th>
<th>G03</th>
<th>L$_1$</th>
<th>L$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N&quot;</td>
<td>-0.107(6)</td>
<td>+0.105(5)</td>
<td>-0.104(3)</td>
<td>+0.098(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N&quot;</td>
<td>-0.025(2)</td>
<td>+0.068(3)</td>
<td>-0.024(1)</td>
<td>+0.057(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C$_2$, N&quot;-C$_2'$</td>
<td>+0.009(1)</td>
<td>-0.006(1)</td>
<td>+0.008(1)</td>
<td>-0.006(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C$_5$, N&quot;-C$_5'$</td>
<td>+0.004(1)</td>
<td>-0.002(1)</td>
<td>+0.003(1)</td>
<td>-0.002(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_2'$-C$_2''$</td>
<td>-0.002(1)</td>
<td>+0.002(1)</td>
<td>-0.002(1)</td>
<td>+0.002(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_1$-C$_4$, C$_1'$-C$_1''$</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$-C$_5$, C$_4'$-C$_4''$</td>
<td>+0.000(1)</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$-C$_5$, C$_2'$-C$_2''$</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N&quot;-C$_2$, N&quot;-C$_5'$</td>
<td>-0.008(1)</td>
<td>+0.007(1)</td>
<td>-0.006(1)</td>
<td>+0.008(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N&quot;-C$_2$, N&quot;-C$_5'$</td>
<td>-0.002(1)</td>
<td>-0.001(1)</td>
<td>-0.003(1)</td>
<td>+0.001(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$-C$_5$, C$_2'$-C$_2''$</td>
<td>-0.001(1)</td>
<td>+0.001(1)</td>
<td>-0.001(1)</td>
<td>+0.001(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_3$-C$_4$, C$_3'$-C$_3''$</td>
<td>+0.002(1)</td>
<td>-0.002(1)</td>
<td>+0.002(1)</td>
<td>-0.002(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\alpha = \angle(C_2', C_2-C_2')$

$\beta = \angle(N'-Co-N) = \angle(N'-Co-N')$

$\gamma = \angle(N'-C_2'-C_2-N) = \angle(N'-C_2'-C_2'-N')$

$\beta' = \angle(N''-Co-N) \uparrow$

$\gamma' = \angle(N''-C_2'-C_2-N) = \angle(N''-C_2'-C_2'-N') \uparrow$

$\uparrow$The C$_{2v}$ symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0$. 

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Table 5 Bond lengths (Å) and angles (deg) in the optimized HS $^4A_2$ and $^4E$ [Co(tpy)$_2$]$_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.

<table>
<thead>
<tr>
<th>Values of the selected structural parameters</th>
<th>Exp.</th>
<th>$^4A_2$</th>
<th>$^4E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ADF</td>
<td>G03</td>
<td>ADF</td>
</tr>
<tr>
<td>Co-N, Co-N'</td>
<td>2.137</td>
<td>2.179(11)</td>
<td>2.185(16)</td>
</tr>
<tr>
<td>Co-N'</td>
<td>2.028</td>
<td>2.054(10)</td>
<td>2.053(19)</td>
</tr>
<tr>
<td>N-C$_2$, N'N''-C$_2$</td>
<td>1.361</td>
<td>1.361(6)</td>
<td>1.356(4)</td>
</tr>
<tr>
<td>N-C$_6$, N'N''-C$_6$</td>
<td>1.331</td>
<td>1.355(23)</td>
<td>1.339(4)</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C''N-C$_3$</td>
<td>1.383</td>
<td>1.401(4)</td>
<td>1.397(3)</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C''-C$_4$</td>
<td>1.380</td>
<td>1.394(4)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C''-C$_5$</td>
<td>1.372</td>
<td>1.395(5)</td>
<td>1.392(3)</td>
</tr>
<tr>
<td>C$_5$-C$_6$, C''-C$_6$</td>
<td>1.380</td>
<td>1.394(4)</td>
<td>1.393(3)</td>
</tr>
<tr>
<td>C$_2$-C$_2$, C$_5$-C$_2$</td>
<td>1.469</td>
<td>1.483(6)</td>
<td>1.483(3)</td>
</tr>
<tr>
<td>N''-C$_2$, N''-Co-N</td>
<td>1.346</td>
<td>1.352(5)</td>
<td>1.347(5)</td>
</tr>
<tr>
<td>N''-C$_5$, N''-Co-N</td>
<td>1.386</td>
<td>1.401(4)</td>
<td>1.398(3)</td>
</tr>
<tr>
<td>C''-C$_4$, C''-C$_5$</td>
<td>1.372</td>
<td>1.394(5)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>$\alpha = \angle$ (C$_6$-C$_5$, C$_2$-C$_2$)</td>
<td>107.5</td>
<td>107.9(3)</td>
<td>107.9(1)</td>
</tr>
<tr>
<td>$\beta = \angle$ (N''-Co-N) = $\angle$ (N''-Co-N')</td>
<td>76.8</td>
<td>76.5(1)</td>
<td>76.6(3)</td>
</tr>
<tr>
<td>$\beta' = \angle$ (N''-Co-N)</td>
<td>153.6</td>
<td>153.1(2)</td>
<td>153.2(6)</td>
</tr>
<tr>
<td>$\gamma = \angle$ (N''-C$_2$-C$_2$-N) = $\angle$ (N''-C$_2$-C$_2$-N')</td>
<td>2.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta = d$ (Co-N')/$d$ (Co-N)</td>
<td>0.949</td>
<td>0.941(2)</td>
<td>0.940(6)</td>
</tr>
</tbody>
</table>

Variations of the parameters on going from the LS $D_{2d}$ to the HS $D_{2d}$ geometries

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ADF</th>
<th>G03</th>
<th>ADF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N''</td>
<td>+0.053</td>
<td>+0.066(4)</td>
<td>+0.066(12)</td>
</tr>
<tr>
<td>Co-N'</td>
<td>+0.116</td>
<td>+0.161(3)</td>
<td>+0.169(3)</td>
</tr>
<tr>
<td>N-C$_2$, N''N''-C$_2$</td>
<td>+0.007</td>
<td>0.000(1)</td>
<td>-0.002(1)</td>
</tr>
<tr>
<td>N-C$_6$, N''N''-C$_6$</td>
<td>-0.019</td>
<td>+0.001(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C''N-C$_3$</td>
<td>+0.007</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C''-C$_4$</td>
<td>+0.002</td>
<td>0.000(1)</td>
<td>0.001(1)</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C''-C$_5$</td>
<td>-0.013</td>
<td>0.000(1)</td>
<td>-0.001(1)</td>
</tr>
<tr>
<td>C$_5$-C$_6$, C''-C$_6$</td>
<td>-0.004</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_2$-C$_2$, C''-C$_2$</td>
<td>-0.011</td>
<td>+0.010(1)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td>N''-C$_2$, N''-C$_6$</td>
<td>-0.004</td>
<td>-0.012(1)</td>
<td>-0.010(1)</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C''N-C$_6$</td>
<td>+0.003</td>
<td>+0.002(1)</td>
<td>+0.001(1)</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C''-C$_6$</td>
<td>-0.007</td>
<td>+0.001(1)</td>
<td>+0.001(1)</td>
</tr>
<tr>
<td>$\alpha = \angle$ (C$_6$-C$_5$, C''-C$_2$)</td>
<td>+1.0</td>
<td>+0.3(1)</td>
<td>+0.5(4)</td>
</tr>
<tr>
<td>$\beta = \angle$ (N''-Co-N) = $\angle$ (N''-Co-N')</td>
<td>-2.7</td>
<td>-3.5(1)</td>
<td>-3.9(1)</td>
</tr>
<tr>
<td>$\beta' = \angle$ (N''-Co-N)</td>
<td>-5.4</td>
<td>-7.0(2)</td>
<td>-7.8(2)</td>
</tr>
<tr>
<td>$\gamma = \angle$ (N''-C$_2$-C$_2$-N) = $\angle$ (N''-C$_2$-C$_2$-N')</td>
<td>+1.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta = d$ (Co-N')/$d$ (Co-N)</td>
<td>0.031</td>
<td>0.047(1)</td>
<td>0.051(4)</td>
</tr>
</tbody>
</table>

$^1$Data are for the geometry of approximate $D_{2d}$ symmetry found in the 295 K X-ray structure of HS [Co(tpy)$_2$](ClO$_4$)$_2$·1.3H$_2$O.$^7$

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

10
Table 6 Bond lengths (Å) and angles (deg) in the optimized HS $^4$A$_2$ and $^4$B$_1$ [Co(ppy)$_2$]$^{2+}$ 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.

<table>
<thead>
<tr>
<th>Values of the selected structural parameters</th>
<th>$^4$A$<em>2$, in C$</em>{2v}$</th>
<th>$^4$B$<em>1$, in C$</em>{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N&quot;</td>
<td>L$_1$</td>
<td>L$_2$</td>
</tr>
<tr>
<td>Co-N&quot;</td>
<td>2.174(19)</td>
<td>2.197(20)</td>
</tr>
<tr>
<td>Co-N&quot;</td>
<td>2.047(17)</td>
<td>2.068(16)</td>
</tr>
<tr>
<td>N-C$_2$, N&quot;-C$_2&quot;$</td>
<td>1.361(7)</td>
<td>1.360(6)</td>
</tr>
<tr>
<td>N-C$_6$, N&quot;-C$_6&quot;$</td>
<td>1.345(5)</td>
<td>1.344(5)</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_2&quot;$-C$_3&quot;$</td>
<td>1.400(4)</td>
<td>1.401(4)</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C$_4&quot;$-C$_4&quot;$</td>
<td>1.394(4)</td>
<td>1.394(4)</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C$_5&quot;$-C$_5&quot;$</td>
<td>1.395(4)</td>
<td>1.395(4)</td>
</tr>
<tr>
<td>C$_5$-C$_6$, C$_6&quot;$-C$_6&quot;$</td>
<td>1.394(4)</td>
<td>1.394(4)</td>
</tr>
<tr>
<td>C$_2$-C$_2'$, C$_6'$-C$_6'$</td>
<td>1.484(5)</td>
<td>1.484(6)</td>
</tr>
<tr>
<td>N'-C$_2'$, N&quot;-C$_6&quot;$</td>
<td>1.351(5)</td>
<td>1.352(5)</td>
</tr>
<tr>
<td>C$_2'$-C$_3'$, C$_3'$-C$_6'$</td>
<td>1.401(4)</td>
<td>1.401(4)</td>
</tr>
<tr>
<td>C$_3'$-C$_4'$, C$_4'$-C$_5'$</td>
<td>1.395(4)</td>
<td>1.394(4)</td>
</tr>
<tr>
<td>$\alpha = \angle$(C$_6'$-C$_2'$, C$_2$-C$_3'$)</td>
<td>107.5(5)</td>
<td>108.2(4)</td>
</tr>
<tr>
<td>$\beta = \angle$(N'-Co-N) = \angle(N&quot;-Co-N&quot;)</td>
<td>76.8(3)</td>
<td>76.2(2)</td>
</tr>
<tr>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N) \superscript{†}</td>
<td>153.6(6)</td>
<td>152.4(4)</td>
</tr>
</tbody>
</table>

Variations associated with the D$_{2d}$ → C$_{2v}$, symmetry lowering: $^4$A$_2$ → $^4$A$_2$ and $^4$E →$^4$B$_1$ ⊕ $^4$B$_2$

<table>
<thead>
<tr>
<th>Variations of $^4$A$<em>2$, in C$</em>{2v}$</th>
<th>L$_1$</th>
<th>L$_2$</th>
<th>Varies versus $^4$B$<em>1$, in C$</em>{2v}$</th>
<th>L$_1$</th>
<th>L$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N&quot;</td>
<td>-0.008(11)</td>
<td>+0.015(11)</td>
<td>$\beta' = \angle$(N'-Co-N) = $\angle$(N&quot;-Co-N')</td>
<td>+0.012(12)</td>
<td>+0.016</td>
</tr>
<tr>
<td>Co-N&quot;</td>
<td>-0.006(8)</td>
<td>+0.015(6)</td>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N') \superscript{†}</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N-C$_2$, N&quot;-C$_2&quot;$</td>
<td>0.000(2)</td>
<td>-0.001(3)</td>
<td>$\beta' = \angle$(N'-Co-N) = $\angle$(N&quot;-Co-N')</td>
<td>0.000(1)</td>
<td>0.000(2)</td>
</tr>
<tr>
<td>N-C$_6$, N&quot;-C$_6&quot;$</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N') \superscript{†}</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_2&quot;$-C$_3&quot;$</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
<td>$\beta' = \angle$(N'-Co-N) = $\angle$(N&quot;-Co-N')</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C$_4&quot;$-C$_4&quot;$</td>
<td>0.001(1)</td>
<td>0.000(1)</td>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N') \superscript{†}</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C$_5&quot;$-C$_5&quot;$</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>$\beta' = \angle$(N'-Co-N) = $\angle$(N&quot;-Co-N')</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_5$-C$_6$, C$_6&quot;$-C$_6&quot;$</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N') \superscript{†}</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_2'$-C$_2'$, C$_6'$-C$_6'$</td>
<td>+0.001(1)</td>
<td>+0.001(1)</td>
<td>$\beta' = \angle$(N'-Co-N) = $\angle$(N&quot;-Co-N')</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>N'-C$_2'$, N&quot;-C$_6&quot;$</td>
<td>-0.001(1)</td>
<td>0.000(1)</td>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N') \superscript{†}</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_2'$-C$_3'$, C$_3'$-C$_6'$</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>$\beta' = \angle$(N'-Co-N) = $\angle$(N&quot;-Co-N')</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
<tr>
<td>C$_3'$-C$_4'$, C$_4'$-C$_5'$</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
<td>$\gamma = \angle$(N'-C$_2$'-C$_2$'-N) = $\angle$(N&quot;-C$_6$&quot;-C$_6$&quot;-N') \superscript{†}</td>
<td>0.000(1)</td>
<td>0.000(1)</td>
</tr>
</tbody>
</table>

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

Table 7 BLYP/\(\omega_b\)–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.

<table>
<thead>
<tr>
<th></th>
<th>LS</th>
<th></th>
<th></th>
<th></th>
<th>LS → HS</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(^2)B(_2)</td>
<td>(^4)A(_2)</td>
<td>(^4)E</td>
<td>(^2)B → (^4)A(_2)</td>
<td>(^2)B → (^4)E</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
</tr>
<tr>
<td>Co-N, Co-N(^\gamma)</td>
<td>2.124</td>
<td>2.189</td>
<td>2.191</td>
<td>0.065</td>
<td>0.067</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N(^\gamma)</td>
<td>1.902</td>
<td>2.063</td>
<td>2.071</td>
<td>0.161</td>
<td>0.169</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C(_2), N(^\alpha)-C(_6)</td>
<td>1.367</td>
<td>1.367</td>
<td>1.364</td>
<td>0.000</td>
<td>-0.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C(_5), N(^\alpha)-C(_6)</td>
<td>1.348</td>
<td>1.349</td>
<td>1.348</td>
<td>0.001</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)-C(_3), C(^\alpha)-C(_3) (^\gamma)</td>
<td>1.403</td>
<td>1.403</td>
<td>1.403</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_3)-C(_4), C(^\alpha)-C(_4) (^\gamma)</td>
<td>1.398</td>
<td>1.397</td>
<td>1.398</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_4)-C(_5), C(^\alpha)-C(_5) (^\gamma)</td>
<td>1.399</td>
<td>1.399</td>
<td>1.398</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_5)-C(_6), C(^\alpha)-C(_6) (^\gamma)</td>
<td>1.398</td>
<td>1.397</td>
<td>1.398</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)-C(_2)' , C(_6)-C(_2)'</td>
<td>1.478</td>
<td>1.488</td>
<td>1.488</td>
<td>0.010</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(^\prime)-C(_2), N(^\prime)-C(_6)</td>
<td>1.369</td>
<td>1.356</td>
<td>1.359</td>
<td>-0.013</td>
<td>-0.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)-C(_3)' , C(_5)-C(_3)'</td>
<td>1.402</td>
<td>1.404</td>
<td>1.403</td>
<td>0.002</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_3)-C(_4)' , C(_5)-C(_4)'</td>
<td>1.397</td>
<td>1.398</td>
<td>1.398</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\alpha = \angle(C\(_6\)-C\(_2\), C\(_5\)-C\(_2\))\) \(107.4\) \(107.6\) \(107.9\) \(0.2\) \(0.5\)

\(\beta = \angle(N\(^\prime\)-Co-N) = \angle(N\(^\alpha\)-Co-N\(^\gamma\))\) \(80.1\) \(76.6\) \(76.2\) \(-3.5\) \(-3.9\)

\(\beta' = \angle(N\(^\alpha\)-Co-N)\) \(160.2\) \(153.3\) \(152.4\) \(-6.9\) \(-7.8\)

\(\gamma = \angle(N\(^\prime\)-C\(_2\)-C\(_2\)-N) = \angle(N\(^\alpha\)-C\(_2\)-C\(_5\)-N\(^\gamma\))\) \(0.0\) \(0.0\) \(0.0\) \(0.0\) \(0.0\)

\(\eta = d(Co-N/Co-N\(^\gamma\))\) \(0.895\) \(0.942\) \(0.945\) \(0.047\) \(0.050\)

\(^\dagger\)The \(D_{2d}\) symmetry constraint imposes that \(\beta' = 2\beta\) and \(\gamma = 0\).

Table 8 OLYP/\(\omega_b\)–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.

<table>
<thead>
<tr>
<th></th>
<th>LS</th>
<th></th>
<th></th>
<th></th>
<th>LS → HS</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(^2)B(_2)</td>
<td>(^4)A(_2)</td>
<td>(^4)E</td>
<td>(^2)B → (^4)A(_2)</td>
<td>(^2)B → (^4)E</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
<td>(L_1), (L_2)</td>
</tr>
<tr>
<td>Co-N, Co-N(^\gamma)</td>
<td>2.118</td>
<td>2.188</td>
<td>2.188</td>
<td>0.070</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N(^\gamma)</td>
<td>1.891</td>
<td>2.057</td>
<td>2.060</td>
<td>0.166</td>
<td>0.169</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C(_2), N(^\alpha)-C(_6)</td>
<td>1.357</td>
<td>1.357</td>
<td>1.356</td>
<td>0.000</td>
<td>-0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-C(_5), N(^\alpha)-C(_6)</td>
<td>1.341</td>
<td>1.341</td>
<td>1.341</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)-C(_3), C(^\alpha)-C(_3) (^\gamma)</td>
<td>1.399</td>
<td>1.399</td>
<td>1.399</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_3)-C(_4), C(^\alpha)-C(_4) (^\gamma)</td>
<td>1.392</td>
<td>1.392</td>
<td>1.392</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_4)-C(_5), C(^\alpha)-C(_5) (^\gamma)</td>
<td>1.393</td>
<td>1.393</td>
<td>1.392</td>
<td>0.000</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_5)-C(_6), C(^\alpha)-C(_6) (^\gamma)</td>
<td>1.392</td>
<td>1.391</td>
<td>1.392</td>
<td>-0.001</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)-C(_2)' , C(_6)-C(_2)'</td>
<td>1.473</td>
<td>1.484</td>
<td>1.484</td>
<td>0.011</td>
<td>0.011</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(^\prime)-C(_2), N(^\prime)-C(_6)</td>
<td>1.361</td>
<td>1.349</td>
<td>1.351</td>
<td>-0.012</td>
<td>-0.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)-C(_3)' , C(_5)-C(_3)'</td>
<td>1.397</td>
<td>1.399</td>
<td>1.399</td>
<td>0.002</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_3)-C(_4)' , C(_5)-C(_4)'</td>
<td>1.391</td>
<td>1.392</td>
<td>1.392</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\alpha = \angle(C\(_6\)-C\(_2\), C\(_5\)-C\(_2\))\) \(107.7\) \(108.0\) \(108.2\) \(0.3\) \(0.5\)

\(\beta = \angle(N\(^\prime\)-Co-N) = \angle(N\(^\alpha\)-Co-N\(^\gamma\))\) \(80.1\) \(76.5\) \(76.3\) \(-3.6\) \(-3.8\)

\(\beta' = \angle(N\(^\alpha\)-Co-N)\) \(160.2\) \(153.0\) \(152.6\) \(-7.2\) \(-7.6\)

\(\gamma = \angle(N\(^\prime\)-C\(_2\)-C\(_2\)-N) = \angle(N\(^\alpha\)-C\(_2\)-C\(_5\)-N\(^\gamma\))\) \(0.0\) \(0.0\) \(0.0\) \(0.0\) \(0.0\)

\(\eta = d(Co-N/Co-N\(^\gamma\))\) \(0.893\) \(0.940\) \(0.941\) \(0.047\) \(0.049\)

\(^\dagger\)The \(D_{2d}\) symmetry constraint imposes that \(\beta' = 2\beta\) and \(\gamma = 0\).
Table 9 OPBE/$\omega$B97X -- optimized LS and HS $[\text{Co(tpy)$_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.

<table>
<thead>
<tr>
<th></th>
<th>LS $^{2}\text{B}_2$</th>
<th>HS $^{2}\text{A}_2$</th>
<th>LS $^{2}\text{E}$</th>
<th>LS $\rightarrow$ HS $^{2}\text{B}_2 \rightarrow ^{2}\text{A}_2$</th>
<th>LS $\rightarrow$ HS $^{2}\text{B}_2 \rightarrow ^{2}\text{E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>2.106</td>
<td>2.173</td>
<td>2.170</td>
<td>0.067</td>
<td>0.064</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.881</td>
<td>2.040</td>
<td>2.053</td>
<td>0.159</td>
<td>0.172</td>
</tr>
<tr>
<td>N-C$_2$, N'-C$_2'$</td>
<td>1.353</td>
<td>1.352</td>
<td>1.350</td>
<td>-0.001</td>
<td>-0.003</td>
</tr>
<tr>
<td>N-C$_6$, N'-C$_6'$</td>
<td>1.337</td>
<td>1.338</td>
<td>1.337</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_2'$-C$_3'$</td>
<td>1.396</td>
<td>1.396</td>
<td>1.395</td>
<td>-0.000</td>
<td>-0.001</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C$_3'$-C$_4'$</td>
<td>1.389</td>
<td>1.388</td>
<td>1.389</td>
<td>-0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C$_4'$-C$_5'$</td>
<td>1.390</td>
<td>1.389</td>
<td>1.390</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>C$_5$-C$_6$, C$_5'$-C$_6'$</td>
<td>1.466</td>
<td>1.476</td>
<td>1.476</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>N'-C$_2$, N'-C$_6'$</td>
<td>1.356</td>
<td>1.345</td>
<td>1.346</td>
<td>-0.011</td>
<td>-0.010</td>
</tr>
<tr>
<td>C$_{2}'$-C$<em>5$, C$</em>{5}'$-C$_5$</td>
<td>1.395</td>
<td>1.396</td>
<td>1.395</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C$_{2}'$-C$<em>4$, C$</em>{4}'$-C$_5$</td>
<td>1.388</td>
<td>1.388</td>
<td>1.388</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$\alpha = \angle(C_6-C_2-C_2-C_2')$
$\beta = \angle(N'-Co-N) = \angle(N''-Co-N')$
$\beta' = \angle(N''-Co-N)$
$\gamma = \angle(N''-C_2'-C_2-N) = \angle(N''-C_5'-C_5'-N')$
$\eta = d(\text{Co-N')}$

$\beta = 2\beta$ and $\gamma = 0$.

Table 10 OPBE/$\omega$B97X -- optimized LS and HS $[\text{Co(tpy)$_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.

<table>
<thead>
<tr>
<th></th>
<th>LS $^{2}\text{B}_2$</th>
<th>HS $^{2}\text{A}_2$</th>
<th>LS $^{2}\text{E}$</th>
<th>LS $\rightarrow$ HS $^{2}\text{B}_2 \rightarrow ^{2}\text{A}_2$</th>
<th>LS $\rightarrow$ HS $^{2}\text{B}_2 \rightarrow ^{2}\text{E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>2.111</td>
<td>2.170</td>
<td>2.171</td>
<td>0.059</td>
<td>0.059</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.889</td>
<td>2.046</td>
<td>2.054</td>
<td>0.157</td>
<td>0.157</td>
</tr>
<tr>
<td>N-C$_2$, N'-C$_2'$</td>
<td>1.360</td>
<td>1.361</td>
<td>1.358</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>N-C$_6$, N'-C$_6'$</td>
<td>1.343</td>
<td>1.345</td>
<td>1.344</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_2'$-C$_3'$</td>
<td>1.395</td>
<td>1.399</td>
<td>1.399</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>C$_3$-C$_4$, C$_3'$-C$_4'$</td>
<td>1.393</td>
<td>1.393</td>
<td>1.394</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C$_4$-C$_5$, C$_4'$-C$_5'$</td>
<td>1.395</td>
<td>1.395</td>
<td>1.395</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C$_5$-C$_6$, C$_5'$-C$_6'$</td>
<td>1.394</td>
<td>1.394</td>
<td>1.395</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C$_2$-C$<em>5$, C$</em>{5}'$-C$_2$</td>
<td>1.471</td>
<td>1.479</td>
<td>1.479</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>N'-C$_2$, N'-C$_6'$</td>
<td>1.362</td>
<td>1.351</td>
<td>1.353</td>
<td>-0.011</td>
<td>-0.011</td>
</tr>
<tr>
<td>C$_2'$-C$_3$, C$_3'$-C$_5$</td>
<td>1.398</td>
<td>1.400</td>
<td>1.399</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>C$_2'$-C$_4$, C$_4'$-C$_5$</td>
<td>1.393</td>
<td>1.394</td>
<td>1.394</td>
<td>0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

$\alpha = \angle(C_6-C_2-C_2-C_2')$
$\beta = \angle(N'-Co-N) = \angle(N''-Co-N')$
$\beta' = \angle(N''-Co-N)$
$\gamma = \angle(N''-C_2'-C_2-N) = \angle(N''-C_5'-C_5'-N')$
$\eta = d(\text{Co-N')}$

$\beta = 2\beta$ and $\gamma = 0$.

$^\dagger$The $D_{2d}$ symmetry constraint imposes that $\beta = 2\beta$ and $\gamma = 0$.
### Table 11 RPBE/$\zeta_f$-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.

<table>
<thead>
<tr>
<th></th>
<th>$^{2}B_2$</th>
<th>$^{4}A_2$</th>
<th>$^{4}E$</th>
<th>$^{2}B_2 \rightarrow ^{4}A_2$</th>
<th>$^{2}B_2 \rightarrow ^{4}E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
</tr>
<tr>
<td>Co-N, Co-N$^\prime$</td>
<td>2.122</td>
<td>2.190</td>
<td>2.189</td>
<td>0.068</td>
<td>0.067</td>
</tr>
<tr>
<td>Co-N$^\prime$</td>
<td>1.899</td>
<td>2.062</td>
<td>2.071</td>
<td>0.163</td>
<td>0.172</td>
</tr>
<tr>
<td>N-C$_2$, N$^{\prime\prime}$-C$_2^\prime$</td>
<td>1.367</td>
<td>1.367</td>
<td>1.364</td>
<td>0.000</td>
<td>-0.003</td>
</tr>
<tr>
<td>N-C$_6$, N$^{\prime\prime}$-C$_6^\prime$</td>
<td>1.349</td>
<td>1.350</td>
<td>1.349</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C$<em>2$-C$<em>3$, C$</em>{2^\prime}$-C$</em>{3^\prime}$</td>
<td>1.405</td>
<td>1.406</td>
<td>1.405</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C$<em>3$-C$<em>4$, C$</em>{3^\prime}$-C$</em>{4^\prime}$</td>
<td>1.399</td>
<td>1.399</td>
<td>1.400</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>C$<em>4$-C$<em>5$, C$</em>{4^\prime}$-C$</em>{5^\prime}$</td>
<td>1.400</td>
<td>1.400</td>
<td>1.400</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C$<em>5$-C$<em>6$, C$</em>{5^\prime}$-C$</em>{6^\prime}$</td>
<td>1.400</td>
<td>1.398</td>
<td>1.400</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>C$<em>2$-C$<em>2^\prime$, C$</em>{2^\prime}$-C$</em>{2^\prime}$</td>
<td>1.479</td>
<td>1.490</td>
<td>1.489</td>
<td>0.011</td>
<td>0.010</td>
</tr>
<tr>
<td>N$^{\prime\prime}$-C$_2^\prime$, N$^\prime$-C$_5^\prime$</td>
<td>1.369</td>
<td>1.357</td>
<td>1.360</td>
<td>-0.012</td>
<td>-0.009</td>
</tr>
<tr>
<td>C$<em>2$-C$<em>2^\prime$, C$</em>{2^\prime}$-C$</em>{5^\prime}$</td>
<td>1.404</td>
<td>1.406</td>
<td>1.405</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>C$<em>2$-C$<em>4^\prime$, C$</em>{2^\prime}$-C$</em>{5^\prime}$</td>
<td>1.399</td>
<td>1.399</td>
<td>1.399</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

$\alpha = \angle(C_6^\prime-C_2^\prime, C_2-C_2^\prime)$ 107.4 107.8 107.9 0.4 0.5
$\beta = \angle(N^\prime$-Co-N) = $\angle(N^\prime$-Co-N$^\prime$) 80.1 76.6 76.2 -3.5 -3.9
$\beta^\prime = \angle(N^\prime$-Co-N) 162.0 153.2 152.3 -7.0 -7.9
$\gamma = \angle(N^\prime$-C$_2^\prime$-C$_2$-N) = $\angle(N^\prime$-C$_6^\prime$-C$_6$-N$^\prime$) 0.0 0.0 0.0 0.0 0.0
$\eta = d$(Co-N$/Co-N^\prime$) 0.895 0.942 0.946 0.047 0.051

$\dagger$The $D_{2d}$ symmetry constraint imposes that $\beta^\prime = 2\beta$ and $\gamma = 0$.

### Table 12 B3LYP/$\zeta$-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.

<table>
<thead>
<tr>
<th></th>
<th>$^{2}B_2$</th>
<th>$^{4}A_2$</th>
<th>$^{4}E$</th>
<th>$^{2}B_2 \rightarrow ^{4}A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
</tr>
<tr>
<td>Co-N, Co-N$^\prime$</td>
<td>2.129</td>
<td>2.187</td>
<td>0.058</td>
<td></td>
</tr>
<tr>
<td>Co-N$^\prime$</td>
<td>1.912</td>
<td>2.068</td>
<td>0.156</td>
<td></td>
</tr>
<tr>
<td>N-C$_2$, N$^{\prime\prime}$-C$_2^\prime$</td>
<td>1.355</td>
<td>1.355</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>N-C$_6$, N$^{\prime\prime}$-C$_6^\prime$</td>
<td>1.336</td>
<td>1.338</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>C$<em>2$-C$<em>3$, C$</em>{2^\prime}$-C$</em>{3^\prime}$</td>
<td>1.394</td>
<td>1.394</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>C$<em>1$-C$<em>4$, C$</em>{1^\prime}$-C$</em>{4^\prime}$</td>
<td>1.390</td>
<td>1.390</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>C$<em>1$-C$<em>5$, C$</em>{1^\prime}$-C$</em>{5^\prime}$</td>
<td>1.390</td>
<td>1.390</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>C$<em>2$-C$<em>6$, C$</em>{2^\prime}$-C$</em>{6^\prime}$</td>
<td>1.390</td>
<td>1.389</td>
<td>-0.001</td>
<td></td>
</tr>
<tr>
<td>C$<em>2$-C$<em>4^\prime$, C$</em>{2^\prime}$-C$</em>{4^\prime}$</td>
<td>1.476</td>
<td>1.486</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>N$^{\prime\prime}$-C$_2$, N$^\prime$-C$_5$</td>
<td>1.353</td>
<td>1.343</td>
<td>-0.010</td>
<td></td>
</tr>
<tr>
<td>C$<em>2$-C$<em>3$, C$</em>{2^\prime}$-C$</em>{3^\prime}$</td>
<td>1.394</td>
<td>1.396</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>C$<em>2$-C$<em>4^\prime$, C$</em>{2^\prime}$-C$</em>{4^\prime}$</td>
<td>1.390</td>
<td>1.391</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>

$\alpha = \angle(C_6^\prime-C_2^\prime, C_2-C_2^\prime)$ 107.6 107.6 0.00
$\beta = \angle(N$-Co-N) = $\angle(N$-Co-N$^\prime$) 79.8 76.5 -3.30
$\beta^\prime = \angle(N^\prime-\text{Co-N})$ 159.6 152.9 -6.70
$\gamma = \angle(N^\prime$-C$_2^\prime$-C$_2$-N) = $\angle(N^\prime$-C$_6^\prime$-C$_6$-N$^\prime$) 0.0 0.0 0.0
$\eta = d$(Co-N$/Co-N^\prime$) 0.898 0.946 0.048

$\dagger$The $D_{2d}$ symmetry constraint imposes that $\beta^\prime = 2\beta$ and $\gamma = 0$. 

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Table 13 B3LYP/6-31G geometries of $D_{2d}$ symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

<table>
<thead>
<tr>
<th></th>
<th>LS $^2\text{B}_2$</th>
<th>HS $^2\text{A}_2$</th>
<th>LS → HS $^2\text{B}_2 \rightarrow ^2\text{A}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^2\text{B}_2$</td>
<td>$^2\text{A}_2$</td>
<td>$^2\text{B}_2 \rightarrow ^2\text{A}_2$</td>
</tr>
<tr>
<td>Co-N, Co-N&quot;</td>
<td>2.142</td>
<td>2.195</td>
<td>0.053</td>
</tr>
<tr>
<td>Co-N&quot;</td>
<td>1.922</td>
<td>2.078</td>
<td>0.156</td>
</tr>
<tr>
<td>N-C_2, N&quot;-C_2&quot;</td>
<td>1.352</td>
<td>1.353</td>
<td>0.001</td>
</tr>
<tr>
<td>N-C_6, N&quot;-C_6&quot;</td>
<td>1.334</td>
<td>1.336</td>
<td>0.002</td>
</tr>
<tr>
<td>C_2-C_3, C_2'-C_3'</td>
<td>1.392</td>
<td>1.393</td>
<td>0.001</td>
</tr>
<tr>
<td>C_2-C_4, C_1'-C_3'</td>
<td>1.389</td>
<td>1.389</td>
<td>0.000</td>
</tr>
<tr>
<td>C_1-C_5, C_2'-C_4'</td>
<td>1.388</td>
<td>1.388</td>
<td>-0.001</td>
</tr>
<tr>
<td>C_5-C_6, C_1'-C_6'</td>
<td>1.478</td>
<td>1.487</td>
<td>0.009</td>
</tr>
<tr>
<td>N'-C_2, N'-C_6'</td>
<td>1.350</td>
<td>1.341</td>
<td>-0.009</td>
</tr>
<tr>
<td>C_2-C_3, C_2'-C_6'</td>
<td>1.393</td>
<td>1.395</td>
<td>0.002</td>
</tr>
<tr>
<td>C_5-C_4', C_5'-C_4'</td>
<td>1.388</td>
<td>1.389</td>
<td>0.001</td>
</tr>
<tr>
<td>α = $\angle(C_6-C_2, C_2-C_2')$</td>
<td>108.0</td>
<td>107.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>β = $\angle(N'-Co-N) = \angle(N&quot;-Co-N')$</td>
<td>79.6</td>
<td>76.2</td>
<td>-3.4</td>
</tr>
<tr>
<td>β' = $\angle(N'-Co-N)$</td>
<td>159.2</td>
<td>152.5</td>
<td>-6.7</td>
</tr>
<tr>
<td>γ = $\angle(N'-C_2'-C_2-N) = \angle(N&quot;-C_6'-C_6'-N')$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>η = d(Co-N'/Co-N&quot;)</td>
<td>0.897</td>
<td>0.947</td>
<td>0.049</td>
</tr>
</tbody>
</table>

The $D_{2d}$ symmetry constraint imposes that $β' = 2β$ and $γ = 0$.

Table 14 HCTH407/6-31G geometries of $D_{2d}$ symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the LS → HS change of states.

<table>
<thead>
<tr>
<th></th>
<th>LS $^2\text{B}_2$</th>
<th>HS $^2\text{A}_2$</th>
<th>LS → HS $^2\text{B}_2 \rightarrow ^2\text{A}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^2\text{B}_2$</td>
<td>$^2\text{A}_2$</td>
<td>$^2\text{B}_2 \rightarrow ^2\text{A}_2$</td>
</tr>
<tr>
<td>Co-N, Co-N&quot;</td>
<td>2.119</td>
<td>2.195</td>
<td>0.076</td>
</tr>
<tr>
<td>Co-N&quot;</td>
<td>1.889</td>
<td>2.051</td>
<td>0.162</td>
</tr>
<tr>
<td>N-C_2, N&quot;-C_2&quot;</td>
<td>1.353</td>
<td>1.352</td>
<td>-0.001</td>
</tr>
<tr>
<td>N-C_6, N&quot;-C_6&quot;</td>
<td>1.335</td>
<td>1.335</td>
<td>0.000</td>
</tr>
<tr>
<td>C_2-C_3, C_2'-C_3'</td>
<td>1.394</td>
<td>1.396</td>
<td>0.002</td>
</tr>
<tr>
<td>C_1-C_4, C_1'-C_4'</td>
<td>1.387</td>
<td>1.387</td>
<td>0.000</td>
</tr>
<tr>
<td>C_1-C_5, C_2'-C_5'</td>
<td>1.388</td>
<td>1.389</td>
<td>0.001</td>
</tr>
<tr>
<td>C_2-C_2', C_2'-C_2'</td>
<td>1.467</td>
<td>1.480</td>
<td>0.013</td>
</tr>
<tr>
<td>N'-C_2, N'-C_6'</td>
<td>1.356</td>
<td>1.344</td>
<td>-0.012</td>
</tr>
<tr>
<td>C_2-C_3, C_4'-C_6'</td>
<td>1.393</td>
<td>1.395</td>
<td>0.002</td>
</tr>
<tr>
<td>C_5-C_4', C_5'-C_4'</td>
<td>1.387</td>
<td>1.388</td>
<td>0.001</td>
</tr>
<tr>
<td>α = $\angle(C_6-C_2, C_2-C_2')$</td>
<td>107.9</td>
<td>108.4</td>
<td>0.5</td>
</tr>
<tr>
<td>β = $\angle(N'-Co-N) = \angle(N&quot;-Co-N')$</td>
<td>80.0</td>
<td>76.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>β' = $\angle(N'-Co-N)$</td>
<td>159.9</td>
<td>153.0</td>
<td>-6.9</td>
</tr>
<tr>
<td>γ = $\angle(N'-C_2'-C_2-N) = \angle(N&quot;-C_6'-C_6'-N')$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>η = d(Co-N'/Co-N&quot;)</td>
<td>0.891</td>
<td>0.934</td>
<td>0.043</td>
</tr>
</tbody>
</table>

The $D_{2d}$ symmetry constraint imposes that $β' = 2β$ and $γ = 0$. 
Table 15 OLYP/\(\beta\) – optimized LS and HS \([\text{Co(tpy)}_2]^{2+}\) geometries of \(D_{2d}\) symmetry: selected bond lengths (\(\AA\)) and angles (deg) and their variations upon the LS \(\rightarrow\) HS change of states.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>LS (\alpha)</th>
<th>HS (\alpha)</th>
<th>LS (\rightarrow) HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Co-N, Co-N'})</td>
<td>2.125</td>
<td>2.201</td>
<td>0.076</td>
</tr>
<tr>
<td>(\text{Co-N'})</td>
<td>1.895</td>
<td>2.056</td>
<td>0.161</td>
</tr>
<tr>
<td>(\text{N-C_2, N''-C_2'})</td>
<td>1.360</td>
<td>1.360</td>
<td>0.000</td>
</tr>
<tr>
<td>(\text{N-C_6, N''-C_6'})</td>
<td>1.343</td>
<td>1.343</td>
<td>0.000</td>
</tr>
<tr>
<td>(\text{C_2-C_3, C_2''-C_3'})</td>
<td>1.400</td>
<td>1.402</td>
<td>0.002</td>
</tr>
<tr>
<td>(\text{C_2-C_4, C_2''-C_4'})</td>
<td>1.393</td>
<td>1.393</td>
<td>0.000</td>
</tr>
<tr>
<td>(\text{C_2-C_5, C_2''-C_5'})</td>
<td>1.394</td>
<td>1.395</td>
<td>0.001</td>
</tr>
<tr>
<td>(\text{C_3-C_6, C_3''-C_6'})</td>
<td>1.394</td>
<td>1.393</td>
<td>-0.001</td>
</tr>
<tr>
<td>(\text{N''-C_2, N''-C_6'})</td>
<td>1.473</td>
<td>1.485</td>
<td>0.012</td>
</tr>
<tr>
<td>(\text{N'-C_2, N'-C_6'})</td>
<td>1.363</td>
<td>1.352</td>
<td>-0.011</td>
</tr>
<tr>
<td>(\text{C_3-C_4, C_3''-C_4'})</td>
<td>1.399</td>
<td>1.401</td>
<td>0.002</td>
</tr>
<tr>
<td>(\text{C_2'-C_2', C_6'-C_6'})</td>
<td>1.393</td>
<td>1.393</td>
<td>0.000</td>
</tr>
<tr>
<td>(\alpha = \angle(\text{C_6-C_2}, \text{C_2-C_2'}))</td>
<td>107.8</td>
<td>108.4</td>
<td>0.6</td>
</tr>
<tr>
<td>(\beta = \angle(N'-\text{Co-N}) = \angle(N''-\text{Co-N'}))</td>
<td>80.0</td>
<td>76.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>(\beta' = \angle(N''-\text{Co-N}))</td>
<td>159.9</td>
<td>153.0</td>
<td>-6.9</td>
</tr>
<tr>
<td>(\gamma = \angle(N''-\text{C_2-C_2'}, \text{N}) = \angle(N''-\text{C_2'-C_6'-N'}))</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\eta = d(\text{Co-N'/Co-N'('})))</td>
<td>0.892</td>
<td>0.934</td>
<td>0.042</td>
</tr>
</tbody>
</table>

\(\dagger\) The \(D_{2d}\) symmetry constraint imposes that \(\beta' = 2\beta\) and \(\gamma = 0\).

Table 16 OPBE/\(\beta\) – optimized LS and HS \([\text{Co(tpy)}_2]^{2+}\) geometries of \(D_{2d}\) symmetry: selected bond lengths (\(\AA\)) and angles (deg) and their variations upon the LS \(\rightarrow\) HS change of states.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>LS (\alpha)</th>
<th>HS (\alpha)</th>
<th>LS (\rightarrow) HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Co-N, Co-N'})</td>
<td>2.087</td>
<td>2.170</td>
<td>0.083</td>
</tr>
<tr>
<td>(\text{Co-N'})</td>
<td>1.869</td>
<td>2.024</td>
<td>0.155</td>
</tr>
<tr>
<td>(\text{N-C_2, N''-C_2'})</td>
<td>1.356</td>
<td>1.355</td>
<td>-0.001</td>
</tr>
<tr>
<td>(\text{N-C_6, N''-C_6'})</td>
<td>1.339</td>
<td>1.339</td>
<td>0.000</td>
</tr>
<tr>
<td>(\text{C_2-C_3, C_2''-C_3'})</td>
<td>1.397</td>
<td>1.398</td>
<td>0.001</td>
</tr>
<tr>
<td>(\text{C_2-C_4, C_2''-C_4'})</td>
<td>1.390</td>
<td>1.391</td>
<td>0.001</td>
</tr>
<tr>
<td>(\text{C_2-C_5, C_2''-C_5'})</td>
<td>1.392</td>
<td>1.392</td>
<td>0.000</td>
</tr>
<tr>
<td>(\text{C_3-C_6, C_3''-C_6'})</td>
<td>1.391</td>
<td>1.390</td>
<td>-0.001</td>
</tr>
<tr>
<td>(\text{N'-C_2, N'-C_6'})</td>
<td>1.467</td>
<td>1.479</td>
<td>0.012</td>
</tr>
<tr>
<td>(\text{N'('')-C_2, N'('')-C_6'})</td>
<td>1.358</td>
<td>1.348</td>
<td>-0.010</td>
</tr>
<tr>
<td>(\text{C_3-C_4, C_3''-C_4'})</td>
<td>1.396</td>
<td>1.398</td>
<td>0.002</td>
</tr>
<tr>
<td>(\text{C_2-C_4', C_2''-C_4'})</td>
<td>1.390</td>
<td>1.391</td>
<td>0.001</td>
</tr>
<tr>
<td>(\alpha = \angle(\text{C_6-C_2}, \text{C_2-C_2'}))</td>
<td>107.0</td>
<td>107.9</td>
<td>0.9</td>
</tr>
<tr>
<td>(\beta = \angle(N'-\text{Co-N}) = \angle(N''-\text{Co-N'}))</td>
<td>80.4</td>
<td>77.0</td>
<td>-3.4</td>
</tr>
<tr>
<td>(\beta' = \angle(N''-\text{Co-N}))</td>
<td>160.8</td>
<td>154.0</td>
<td>-6.8</td>
</tr>
<tr>
<td>(\gamma = \angle(N''-\text{C_2-C_2'}, \text{N}) = \angle(N''-\text{C_2'-C_6'-N'}))</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\eta = d(\text{Co-N'/Co-N'('})))</td>
<td>0.896</td>
<td>0.933</td>
<td>0.037</td>
</tr>
</tbody>
</table>

\(\dagger\) The \(D_{2d}\) symmetry constraint imposes that \(\beta' = 2\beta\) and \(\gamma = 0\).
**Table 17** PBE/\$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.

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>LS $^2$B₂</th>
<th>HS $^2$A₂</th>
<th>LS $\rightarrow$ HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>2.090</td>
<td>2.160</td>
<td>0.070</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.885</td>
<td>2.039</td>
<td>0.154</td>
</tr>
<tr>
<td>N-C₂, N''-C₂'</td>
<td>1.363</td>
<td>1.362</td>
<td>-0.001</td>
</tr>
<tr>
<td>N-C₆, N''-C₆'</td>
<td>1.344</td>
<td>1.344</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.399</td>
<td>1.400</td>
<td>0.001</td>
</tr>
<tr>
<td>C₁-C₄, C₁'-C₄'</td>
<td>1.395</td>
<td>1.395</td>
<td>0.000</td>
</tr>
<tr>
<td>C₄-C₅, C₄'-C₅'</td>
<td>1.396</td>
<td>1.396</td>
<td>0.000</td>
</tr>
<tr>
<td>C₅-C₆, C₅'-C₆'</td>
<td>1.395</td>
<td>1.394</td>
<td>-0.001</td>
</tr>
<tr>
<td>C₂-C₂', C₆'-C₆'</td>
<td>1.470</td>
<td>1.481</td>
<td>0.011</td>
</tr>
<tr>
<td>N'-C₄', N''-C₄''</td>
<td>1.364</td>
<td>1.352</td>
<td>-0.012</td>
</tr>
<tr>
<td>C₂-C₃, C₃'-C₆'</td>
<td>1.399</td>
<td>1.401</td>
<td>0.002</td>
</tr>
<tr>
<td>C₃'-C₄, C₄'-C₅'</td>
<td>1.395</td>
<td>1.396</td>
<td>0.001</td>
</tr>
<tr>
<td>$\alpha$ = $\angle$(C₆'-C₂', C₂-C₂')</td>
<td>106.6</td>
<td>107.1</td>
<td>0.5</td>
</tr>
<tr>
<td>$\beta$ = $\angle$(N'-Co-N) = $\angle$(N''-Co-N')</td>
<td>80.3</td>
<td>77.0</td>
<td>-3.3</td>
</tr>
<tr>
<td>$\beta'$ = $\angle$(N''-Co-N) \text{‡}</td>
<td>160.7</td>
<td>154.0</td>
<td>-6.7</td>
</tr>
<tr>
<td>$\gamma$ = $\angle$(N'-C₄'-C₂') = $\angle$(N''-C₄''-C₆'-N'') \text{‡}</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta$ = d(Co-N'/Co-N'')</td>
<td>0.902</td>
<td>0.944</td>
<td>0.042</td>
</tr>
</tbody>
</table>

\text{‡}The $D_{2d}$ symmetry constraint imposes that $\beta' = 2\beta$ and $\gamma = 0.$
Table 18 BLYP/\(\mathcal{Z}_k\)-optimized LS and HS [Co(py)_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: \(^2\!)_2 \rightarrow \(^2\!\)A_1; HS: \(^4\!\)A_2 \rightarrow \(^4\!\)A_2 and \(^4\!\)E \rightarrow \(^4\!\)B_1 \oplus \(^4\!\)B_2).

<table>
<thead>
<tr>
<th>Parameters values in the (C_{2v}) geometries</th>
<th>LS (^2!)A_1</th>
<th>HS (^4!)A_2</th>
<th>HS (^4!)B_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>L_1</td>
<td>L_2</td>
<td>L_1</td>
</tr>
<tr>
<td>2.017</td>
<td>2.232</td>
<td>2.187</td>
<td>2.210</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.877</td>
<td>1.971</td>
<td>2.064</td>
</tr>
<tr>
<td>N-C_2, N'(\prime)-C_2'</td>
<td>1.376</td>
<td>1.360</td>
<td>1.367</td>
</tr>
<tr>
<td>N-C_6, N'(\prime)-C_6'</td>
<td>1.352</td>
<td>1.346</td>
<td>1.349</td>
</tr>
<tr>
<td>C_2-C_3, C_2'-C_2'</td>
<td>1.400</td>
<td>1.405</td>
<td>1.402</td>
</tr>
<tr>
<td>C_1-C_4, C_1'-C_4'</td>
<td>1.397</td>
<td>1.398</td>
<td>1.398</td>
</tr>
<tr>
<td>C_1-C_5, C_1'-C_5'</td>
<td>1.399</td>
<td>1.398</td>
<td>1.398</td>
</tr>
<tr>
<td>C_1-C_6, C_1'-C_6'</td>
<td>1.397</td>
<td>1.398</td>
<td>1.397</td>
</tr>
<tr>
<td>C_1-C_2', C_1'-C_6'</td>
<td>1.470</td>
<td>1.485</td>
<td>1.488</td>
</tr>
<tr>
<td>N'=C_2', N'=C_6'</td>
<td>1.366</td>
<td>1.368</td>
<td>1.355</td>
</tr>
<tr>
<td>C_2-C_3', C_2'-C_6'</td>
<td>1.401</td>
<td>1.403</td>
<td>1.404</td>
</tr>
<tr>
<td>C_3-C_4', C_3'-C_4'</td>
<td>1.400</td>
<td>1.396</td>
<td>1.398</td>
</tr>
<tr>
<td>(\alpha = \angle(C_2'-C_6', C_2-C_3'))</td>
<td>103.4</td>
<td>110.8</td>
<td>107.6</td>
</tr>
<tr>
<td>(\beta = \angle(N'-Co-N) = \angle(N'^{\prime}-Co-N'))</td>
<td>81.3</td>
<td>78.0</td>
<td>76.6</td>
</tr>
<tr>
<td>(\beta' = \angle(N'^{\prime}-Co-N'))</td>
<td>162.6</td>
<td>156.0</td>
<td>153.3</td>
</tr>
<tr>
<td>(\gamma = \angle(N'-C_2'-C_2-N) = \angle(N'^{\prime}-C_6'-C_6'-N'))</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\eta = d(Co-N'/Co-N'))</td>
<td>0.931</td>
<td>0.883</td>
<td>0.944</td>
</tr>
</tbody>
</table>

Variations associated with the \(D_{2d} \rightarrow C_{2v}\) symmetry lowering

<table>
<thead>
<tr>
<th>Parameters values in the (C_{2v}) geometries</th>
<th>LS (^2!)A_1</th>
<th>HS (^4!)A_2</th>
<th>HS (^4!)B_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>-0.107</td>
<td>0.108</td>
<td>-0.002</td>
</tr>
<tr>
<td>Co-N'</td>
<td>-0.025</td>
<td>0.069</td>
<td>0.001</td>
</tr>
<tr>
<td>N-C_2, N'-C_6'</td>
<td>0.009</td>
<td>-0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>N-C_6, N'-C_6'</td>
<td>0.004</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>C_2-C_3, C_2'-C_2'</td>
<td>-0.003</td>
<td>0.002</td>
<td>-0.001</td>
</tr>
<tr>
<td>C_1-C_4, C_1'-C_4'</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>C_1-C_5, C_1'-C_5'</td>
<td>0.000</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>C_1-C_6, C_1'-C_6'</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C_1-C_2', C_1'-C_6'</td>
<td>0.008</td>
<td>0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>N'=C_2', N'=C_6'</td>
<td>0.003</td>
<td>0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>C_2-C_3', C_2'-C_6'</td>
<td>-0.001</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C_3-C_4', C_3'-C_4'</td>
<td>0.003</td>
<td>-0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>(\alpha = \angle(C_2'-C_2', C_2-C_3'))</td>
<td>-4.0</td>
<td>3.4</td>
<td>0.0</td>
</tr>
<tr>
<td>(\beta = \angle(N'-Co-N) = \angle(N'^{\prime}-Co-N'))</td>
<td>1.2</td>
<td>-2.1</td>
<td>0.0</td>
</tr>
<tr>
<td>(\beta' = \angle(N'^{\prime}-Co-N'))</td>
<td>2.4</td>
<td>4.2</td>
<td>0.0</td>
</tr>
<tr>
<td>(\gamma = \angle(N'-C_2'-C_2-N) = \angle(N'^{\prime}-C_6'-C_6'-N'))</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\eta = d(Co-N'/Co-N'))</td>
<td>0.035</td>
<td>0.012</td>
<td>0.001</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) The \(D_{2d}\) and \(C_{2v}\) symmetry constraints impose that \(\beta' = 2\beta\) and \(\gamma = 0\).
Table 19 OLYP/\( \beta \)–optimized LS and HS [Co(py)\(_2\)]\(^{2+} \) geometries of C\(_{2v} \) symmetry: selected bond lengths (\( \text{Å} \)) and angles (deg) and their variations upon the \( D_{2d} \rightarrow C_{2v} \) symmetry lowering (LS: \( 2^2B_2 \rightarrow 2^2A_1 \); HS: \( 4^2A_2 \rightarrow 4^2A_2 \) and \( 4^2E \rightarrow 4^2B_1 \oplus 4^2B_2 \)).

<table>
<thead>
<tr>
<th>Parameters in the C(_{2v} ) geometries</th>
<th>LS ( ^2A_1 )</th>
<th>HS ( ^4A_2 )</th>
<th>HS ( ^4B_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L(_1)</td>
<td>L(_2)</td>
<td>L(_1)</td>
</tr>
<tr>
<td>Co-N, Co-N(^#)</td>
<td>2.020</td>
<td>2.221</td>
<td>2.195</td>
</tr>
<tr>
<td>Co-N(^\prime)</td>
<td>1.870</td>
<td>1.956</td>
<td>2.059</td>
</tr>
<tr>
<td>N-C(_2), N(^#)-C(_2)(^#)</td>
<td>1.366</td>
<td>1.352</td>
<td>1.357</td>
</tr>
<tr>
<td>N-C(_6), N(^#)-C(_6)(^#)</td>
<td>1.345</td>
<td>1.339</td>
<td>1.342</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_2)-C(_3)(^#)</td>
<td>1.397</td>
<td>1.401</td>
<td>1.399</td>
</tr>
<tr>
<td>C(_1)-C(_4), C(_1)-C(_4)(^#)</td>
<td>1.391</td>
<td>1.392</td>
<td>1.392</td>
</tr>
<tr>
<td>C(_1)-C(_5), C(_1)-C(_5)(^#)</td>
<td>1.393</td>
<td>1.392</td>
<td>1.393</td>
</tr>
<tr>
<td>C(_1)-C(_6), C(_1)-C(_6)(^#)</td>
<td>1.392</td>
<td>1.394</td>
<td>1.392</td>
</tr>
<tr>
<td>C(_2)-C(_2), C(_2)-C(_2)(^#)</td>
<td>1.465</td>
<td>1.480</td>
<td>1.483</td>
</tr>
<tr>
<td>N(^#)-C(_2), N(^#)-C(_2)(^#)</td>
<td>1.359</td>
<td>1.361</td>
<td>1.349</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_2)-C(_3)(^#)</td>
<td>1.397</td>
<td>1.399</td>
<td>1.399</td>
</tr>
<tr>
<td>C(_2)-C(_4), C(_2)-C(_4)(^#)</td>
<td>1.392</td>
<td>1.389</td>
<td>1.392</td>
</tr>
<tr>
<td>( \alpha = \angle(C(_2)-C(_2)-C(_2)) )</td>
<td>104.0</td>
<td>111.0</td>
<td>108.3</td>
</tr>
<tr>
<td>( \beta = \angle(N(^#)-Co-N) = \angle(N(^#)-Co-N(^\prime)) )</td>
<td>81.1</td>
<td>78.0</td>
<td>76.4</td>
</tr>
<tr>
<td>( \beta' = \angle(N(^#)-Co-N) )</td>
<td>162.1</td>
<td>156.1</td>
<td>152.8</td>
</tr>
<tr>
<td>( \gamma = \angle(N(^#)-C(_2)-C(_3)-N) = \angle(N(^#)-C(_2)-C(_6)-N) )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \eta = d(Co-N(^#)-Co-N(^#)) )</td>
<td>0.926</td>
<td>0.881</td>
<td>0.938</td>
</tr>
</tbody>
</table>

Variations associated with the \( D_{2d} \rightarrow C_{2v} \) symmetry lowering

<table>
<thead>
<tr>
<th>Parameters in the C(_{2v} ) geometries</th>
<th>LS ( ^2A_1 )</th>
<th>HS ( ^4A_2 )</th>
<th>HS ( ^4B_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L(_1)</td>
<td>L(_2)</td>
<td>L(_1)</td>
</tr>
<tr>
<td>Co-N, Co-N(^#)</td>
<td>-0.098</td>
<td>0.103</td>
<td>0.007</td>
</tr>
<tr>
<td>Co-N(^\prime)</td>
<td>-0.021</td>
<td>0.065</td>
<td>0.002</td>
</tr>
<tr>
<td>N-C(_2), N(^#)-C(_2)(^#)</td>
<td>0.009</td>
<td>-0.005</td>
<td>0.000</td>
</tr>
<tr>
<td>N-C(_6), N(^#)-C(_6)(^#)</td>
<td>0.004</td>
<td>-0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_2)-C(_3)(^#)</td>
<td>-0.002</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_1)-C(_4), C(_1)-C(_4)(^#)</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_1)-C(_5), C(_1)-C(_5)(^#)</td>
<td>0.000</td>
<td>-0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_1)-C(_6), C(_1)-C(_6)(^#)</td>
<td>0.000</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>C(_2)-C(_2), C(_2)-C(_2)(^#)</td>
<td>-0.008</td>
<td>0.007</td>
<td>-0.001</td>
</tr>
<tr>
<td>N(^#)-C(_2), N(^#)-C(_2)(^#)</td>
<td>-0.002</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_2)-C(_3)(^#)</td>
<td>0.000</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_2)-C(_4), C(_2)-C(_4)(^#)</td>
<td>0.001</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>( \alpha = \angle(C(_2)-C(_2)-C(_2)) )</td>
<td>-3.7</td>
<td>3.3</td>
<td>0.3</td>
</tr>
<tr>
<td>( \beta = \angle(N(^#)-Co-N) = \angle(N(^#)-Co-N(^\prime)) )</td>
<td>1.0</td>
<td>-2.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>( \beta' = \angle(N(^#)-Co-N) )</td>
<td>1.9</td>
<td>-4.1</td>
<td>-0.2</td>
</tr>
<tr>
<td>( \gamma = \angle(N(^#)-C(_2)-C(_3)-N) = \angle(N(^#)-C(_2)-C(_6)-N) )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \eta = d(Co-N(^#)-Co-N(^#)) )</td>
<td>0.033</td>
<td>-0.012</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

\(^\dagger\)The \( D_{2d} \) and \( C_{2v} \) symmetry constraints impose that \( \beta' = 2\beta \) and \( \gamma = 0 \).
Table 20 OPBE/$\gamma$-optimized LS and HS $[\text{Co(py)}_2]^2^+$ geometries of $C_{2v}$ symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the $D_{2d} \rightarrow C_{2v}$ symmetry lowering ($\text{LS}: 2B_2 \rightarrow 2A_1$; $\text{HS}: 4A_2 \rightarrow 4A_2$ and $4E \rightarrow 4B_1 \oplus 4B_2$).

<table>
<thead>
<tr>
<th>Parameters values in the $C_{2v}$ geometries</th>
<th>LS $^2A_1$</th>
<th>HS $^4A_2$</th>
<th>HS $^4B_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N''</td>
<td>1.998</td>
<td>2.216</td>
<td>2.155</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.854</td>
<td>1.953</td>
<td>2.027</td>
</tr>
<tr>
<td>N-C2, N''-C'$_2$</td>
<td>1.361</td>
<td>1.346</td>
<td>1.352</td>
</tr>
<tr>
<td>N-C6, N''-C'$_6$</td>
<td>1.341</td>
<td>1.335</td>
<td>1.338</td>
</tr>
<tr>
<td>C2-C3, C''$_2$-C'$_3$</td>
<td>1.394</td>
<td>1.397</td>
<td>1.395</td>
</tr>
<tr>
<td>C1-C4, C''$_1$-C'$_4$</td>
<td>1.388</td>
<td>1.388</td>
<td>1.389</td>
</tr>
<tr>
<td>C1-C5, C''$_1$-C'$_5$</td>
<td>1.390</td>
<td>1.389</td>
<td>1.390</td>
</tr>
<tr>
<td>C2-C6, C'$_2$-C'$_6$</td>
<td>1.389</td>
<td>1.391</td>
<td>1.389</td>
</tr>
<tr>
<td>C2-C'$_2$, C'$_2$-C'$_2$</td>
<td>1.459</td>
<td>1.474</td>
<td>1.478</td>
</tr>
<tr>
<td>N''-C''$_2$, N''-C''$_2$</td>
<td>1.354</td>
<td>1.355</td>
<td>1.344</td>
</tr>
<tr>
<td>C2-C''$_3$, C'$_3$-C'$_6$</td>
<td>1.394</td>
<td>1.396</td>
<td>1.396</td>
</tr>
<tr>
<td>C3-C''$_4$, C'$_4$-C'$_4$</td>
<td>1.389</td>
<td>1.386</td>
<td>1.389</td>
</tr>
<tr>
<td>$\alpha = \angle (C'_2$-C'$_2$, C$_2$-C$_2$)</td>
<td>103.6</td>
<td>111.2</td>
<td>107.4</td>
</tr>
<tr>
<td>$\beta = \angle (N''$-Co-N) = \angle (N''$-Co-N')</td>
<td>81.3</td>
<td>77.8</td>
<td>76.9</td>
</tr>
<tr>
<td>$\beta' = \angle (N''$-Co-N) $^\dagger$</td>
<td>162.5</td>
<td>155.7</td>
<td>153.9</td>
</tr>
<tr>
<td>$\gamma = \angle (N''$-C'$_2$-C''$_2$-N')</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta = d$(Co-N'/Co-N'')</td>
<td>0.928</td>
<td>0.881</td>
<td>0.941</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variations associated with the $D_{2d} \rightarrow C_{2v}$ symmetry lowering</th>
<th>LS $^2A_1$</th>
<th>HS $^4A_2$</th>
<th>HS $^4B_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N''</td>
<td>-0.108</td>
<td>0.110</td>
<td>-0.018</td>
</tr>
<tr>
<td>Co-N'</td>
<td>-0.027</td>
<td>0.072</td>
<td>-0.013</td>
</tr>
<tr>
<td>N-C2, N''-C'$_2$</td>
<td>0.008</td>
<td>-0.007</td>
<td>0.000</td>
</tr>
<tr>
<td>N-C6, N''-C'$_6$</td>
<td>0.004</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>C2-C3, C''$_2$-C'$_3$</td>
<td>-0.002</td>
<td>0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>C1-C4, C''$_1$-C'$_4$</td>
<td>-0.001</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>C1-C5, C''$_1$-C'$_5$</td>
<td>0.000</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>C2-C6, C'$_2$-C'$_6$</td>
<td>-0.001</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C2-C'$_2$, C'$_2$-C'$_2$</td>
<td>-0.007</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td>N''-C''$_2$, N''-C''$_2$</td>
<td>-0.002</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>C2-C''$_3$, C'$_3$-C'$_6$</td>
<td>-0.001</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C3-C''$_4$, C'$_4$-C'$_4$</td>
<td>0.001</td>
<td>-0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>$\alpha = \angle (C''$_2$-C''$_2$, C$_2$-C$_2$)</td>
<td>-4.1</td>
<td>3.5</td>
<td>-0.6</td>
</tr>
<tr>
<td>$\beta = \angle (N''$-Co-N) = \angle (N''$-Co-N')</td>
<td>1.3</td>
<td>-2.2</td>
<td>0.4</td>
</tr>
<tr>
<td>$\beta' = \angle (N''$-Co-N) $^\dagger$</td>
<td>2.5</td>
<td>-4.3</td>
<td>0.8</td>
</tr>
<tr>
<td>$\gamma = \angle (N''$-C''$_2$-C''$_2$-N') $^\dagger$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta = d$(Co-N'/Co-N'')</td>
<td>0.035</td>
<td>-0.012</td>
<td>0.002</td>
</tr>
</tbody>
</table>

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

20
Table 21 PBE/\(\mathcal{H}_{\text{f}}\) – 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 \(^4E \rightarrow ^3B_1 \oplus ^3B_2\)).

<table>
<thead>
<tr>
<th>Parameters values in the (C_{2v}) geometries</th>
<th>(^2A_1) L1</th>
<th>(^2A_1) L2</th>
<th>(^4A_2) L1</th>
<th>(^4A_2) L2</th>
<th>(^3B_1) L1</th>
<th>(^3B_1) L2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N(^\alpha)</td>
<td>1.997</td>
<td>2.209</td>
<td>2.152</td>
<td>2.173</td>
<td>2.145</td>
<td>2.172</td>
</tr>
<tr>
<td>Co-N(^\beta)</td>
<td>1.862</td>
<td>1.955</td>
<td>2.032</td>
<td>2.053</td>
<td>2.087</td>
<td>2.050</td>
</tr>
<tr>
<td>N-C(_2), N(^\alpha)-C(_2)(^\alpha)</td>
<td>1.370</td>
<td>1.355</td>
<td>1.361</td>
<td>1.360</td>
<td>1.358</td>
<td>1.359</td>
</tr>
<tr>
<td>N-C(_6), N(^\alpha)-C(_6)(^\alpha)</td>
<td>1.347</td>
<td>1.342</td>
<td>1.345</td>
<td>1.344</td>
<td>1.345</td>
<td>1.342</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_2)-C(_3)(^\alpha)</td>
<td>1.396</td>
<td>1.400</td>
<td>1.398</td>
<td>1.399</td>
<td>1.399</td>
<td>1.398</td>
</tr>
<tr>
<td>C(_3)-C(_4), C(_4)-C(_5)(^\alpha)</td>
<td>1.393</td>
<td>1.393</td>
<td>1.394</td>
<td>1.394</td>
<td>1.393</td>
<td>1.395</td>
</tr>
<tr>
<td>C(_4)-C(_5), C(_5)-C(_6)(^\alpha)</td>
<td>1.395</td>
<td>1.395</td>
<td>1.395</td>
<td>1.395</td>
<td>1.394</td>
<td>1.395</td>
</tr>
<tr>
<td>C(_5)-C(_6), C(_6)-C(_2)(^\alpha)</td>
<td>1.394</td>
<td>1.395</td>
<td>1.394</td>
<td>1.395</td>
<td>1.393</td>
<td>1.395</td>
</tr>
<tr>
<td>N(^\prime)-C(_2), N(^\prime)-C(_2)(^\alpha)</td>
<td>1.462</td>
<td>1.476</td>
<td>1.480</td>
<td>1.480</td>
<td>1.475</td>
<td>1.483</td>
</tr>
<tr>
<td>N(^\prime)-C(_6), N(^\prime)-C(_6)(^\alpha)</td>
<td>1.360</td>
<td>1.361</td>
<td>1.350</td>
<td>1.351</td>
<td>1.351</td>
<td>1.352</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_3)-C(_6)(^\alpha)</td>
<td>1.397</td>
<td>1.399</td>
<td>1.400</td>
<td>1.400</td>
<td>1.399</td>
<td>1.399</td>
</tr>
<tr>
<td>C(_4)-C(_5), C(_5)-C(_6)(^\alpha)</td>
<td>1.396</td>
<td>1.392</td>
<td>1.395</td>
<td>1.395</td>
<td>1.394</td>
<td>1.395</td>
</tr>
</tbody>
</table>

\[\alpha = \angle(C\(_2\)-C\(_2\)-C\(_2\))\]
\[\beta = \angle(N\(^\prime\)-Co-N) = \angle(N\(^\prime\)-Co-N\(^\alpha\))\]
\[\beta' = \angle(N\(^\prime\)-Co-N)\]\n\[\gamma = \angle(N\(^\prime\)-C\(_2\)-C\(_2\)-N) = \angle(N\(^\prime\)-C\(_2\)-C\(_6\)-N\(^\alpha\))\]\n\[\eta = d(Co-N\(^\prime\)/Co-N\(^\alpha\))\]

Variations associated with the \(D_{2d} \rightarrow C_{2v}\) symmetry lowering

<table>
<thead>
<tr>
<th>Parameters values in the (C_{2v}) geometries</th>
<th>(^2A_1) L1</th>
<th>(^2A_1) L2</th>
<th>(^4A_2) L1</th>
<th>(^4A_2) L2</th>
<th>(^3B_1) L1</th>
<th>(^3B_1) L2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N(^\alpha)</td>
<td>-0.114</td>
<td>0.098</td>
<td>-0.018</td>
<td>0.003</td>
<td>-0.026</td>
<td>0.001</td>
</tr>
<tr>
<td>Co-N(^\beta)</td>
<td>-0.027</td>
<td>0.066</td>
<td>-0.014</td>
<td>0.007</td>
<td>0.033</td>
<td>-0.004</td>
</tr>
<tr>
<td>N-C(_2), N(^\alpha)-C(_2)(^\alpha)</td>
<td>0.010</td>
<td>-0.005</td>
<td>0.000</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>N-C(_6), N(^\alpha)-C(_6)(^\alpha)</td>
<td>0.004</td>
<td>-0.001</td>
<td>0.000</td>
<td>-0.001</td>
<td>0.001</td>
<td>-0.002</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_2)-C(_3)(^\alpha)</td>
<td>-0.002</td>
<td>0.002</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.001</td>
</tr>
<tr>
<td>C(_3)-C(_4), C(_4)-C(_5)(^\alpha)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.001</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>C(_4)-C(_5), C(_5)-C(_6)(^\alpha)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_5)-C(_6), C(_6)-C(_2)(^\alpha)</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_3)-C(_6)(^\alpha)</td>
<td>-0.009</td>
<td>0.005</td>
<td>0.001</td>
<td>0.000</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>N(^\prime)-C(_2), N(^\prime)-C(_2)(^\alpha)</td>
<td>-0.002</td>
<td>-0.001</td>
<td>-0.001</td>
<td>0.000</td>
<td>-0.002</td>
<td>-0.001</td>
</tr>
<tr>
<td>N(^\prime)-C(_6), N(^\prime)-C(_6)(^\alpha)</td>
<td>-0.001</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C(_2)-C(_3), C(_3)-C(_6)(^\alpha)</td>
<td>0.003</td>
<td>-0.001</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\[\alpha = \angle(C\(_2\)-C\(_2\)-C\(_2\))\]
\[\beta = \angle(N\(^\prime\)-Co-N) = \angle(N\(^\prime\)-Co-N\(^\alpha\))\]
\[\beta' = \angle(N\(^\prime\)-Co-N)\]
\[\gamma = \angle(N\(^\prime\)-C\(_2\)-C\(_2\)-N) = \angle(N\(^\prime\)-C\(_2\)-C\(_6\)-N\(^\alpha\))\]
\[\eta = d(Co-N\(^\prime\)/Co-N\(^\alpha\))\]

\(^\dagger\)The \(D_{2d}\) and \(C_{2v}\) symmetry constraints impose that \(\beta' = 2\beta\) and \(\gamma = 0\).
Table 22 RPBE/\(\gamma_{fc}\)–optimized LS and HS \([\text{Co(tpy)}_2]^{2+}\) 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: \(^2\text{A}_1\); HS: \(^4\text{A}_2\) → \(^4\text{A}_2\) and \(^4\text{E} \rightarrow ^4\text{B}_1 \oplus ^4\text{B}_2\)).

<table>
<thead>
<tr>
<th>Parameters values in the (C_{2v}) geometries</th>
<th>LS (^2\text{A}_1)</th>
<th>HS (^4\text{A}_2)</th>
<th>HS (^4\text{B}_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>2.014 2.230</td>
<td>2.179 2.220</td>
<td>2.189 2.212</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.874 1.969</td>
<td>2.054 2.081</td>
<td>2.118 2.064</td>
</tr>
<tr>
<td>N-C2, N'c-C'2</td>
<td>1.375 1.360</td>
<td>1.368 1.366</td>
<td>1.362 1.366</td>
</tr>
<tr>
<td>N-C6, N'c-C'6</td>
<td>1.353 1.347</td>
<td>1.350 1.349</td>
<td>1.348 1.347</td>
</tr>
<tr>
<td>C2-C3, C'2-C'3</td>
<td>1.403 1.407</td>
<td>1.404 1.406</td>
<td>1.403 1.404</td>
</tr>
<tr>
<td>C1-C4, C'1-C'4</td>
<td>1.399 1.399</td>
<td>1.399 1.398</td>
<td>1.399 1.400</td>
</tr>
<tr>
<td>C1-C5, C'1-C'5</td>
<td>1.400 1.400</td>
<td>1.400 1.400</td>
<td>1.400 1.397</td>
</tr>
<tr>
<td>C2-C6, C'2-C'6</td>
<td>1.399 1.400</td>
<td>1.398 1.398</td>
<td>1.399 1.400</td>
</tr>
<tr>
<td>C2-C2', C'6-C'2</td>
<td>1.471 1.487</td>
<td>1.491 1.491</td>
<td>1.483 1.493</td>
</tr>
<tr>
<td>N'-C'2, N'C'2</td>
<td>1.367 1.368</td>
<td>1.356 1.358</td>
<td>1.357 1.361</td>
</tr>
<tr>
<td>C2-C3', C'6-C'6</td>
<td>1.403 1.405</td>
<td>1.405 1.405</td>
<td>1.405 1.405</td>
</tr>
<tr>
<td>C1-C4', C'1-C'4</td>
<td>1.401 1.397</td>
<td>1.399 1.399</td>
<td>1.398 1.399</td>
</tr>
</tbody>
</table>

\(\alpha = \angle(\text{C}_6'-\text{C}_2'-\text{C}_2-\text{C}_2)\)
\(\beta = \angle(\text{N'}-\text{Co}-\text{N}) = \angle(\text{N'}-\text{Co}-\text{N}')\)
\(\gamma = \angle(\text{N}^\prime-\text{C}_{2}^\prime-\text{C}_{2}-\text{N}) = \angle(\text{N}^\prime-\text{C}_{2}^\prime-\text{C}_{6}^\prime-\text{N})\)
\(\eta = d(\text{Co-N'/Co-N'})\)

<table>
<thead>
<tr>
<th>Variations associated with the (D_{2d} \rightarrow C_{2v}) symmetry lowering</th>
<th>LS</th>
<th>HS</th>
<th>HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N, Co-N'</td>
<td>-0.108 0.108</td>
<td>-0.011 0.030</td>
<td>0.000 0.023</td>
</tr>
<tr>
<td>Co-N'</td>
<td>-0.025 0.070</td>
<td>-0.008 0.019</td>
<td>0.047 0.007</td>
</tr>
<tr>
<td>N-C2, N'c-C'2</td>
<td>0.008 -0.007</td>
<td>0.001 -0.001</td>
<td>-0.002 0.002</td>
</tr>
<tr>
<td>N-C6, N'c-C'6</td>
<td>0.004 -0.002</td>
<td>0.000 -0.001</td>
<td>-0.001 0.002</td>
</tr>
<tr>
<td>C2-C3, C'2-C'3</td>
<td>-0.002 0.002</td>
<td>-0.002 0.000</td>
<td>-0.002 -0.001</td>
</tr>
<tr>
<td>C1-C4, C'1-C'4</td>
<td>0.000 0.000</td>
<td>0.000 -0.001</td>
<td>0.000 0.000</td>
</tr>
<tr>
<td>C1-C5, C'1-C'5</td>
<td>0.000 0.000</td>
<td>0.000 0.000</td>
<td>0.000 0.000</td>
</tr>
<tr>
<td>C2-C6, C'2-C'6</td>
<td>-0.001 0.000</td>
<td>0.000 0.000</td>
<td>-0.001 0.000</td>
</tr>
<tr>
<td>C2-C2', C'6-C'2</td>
<td>-0.008 0.008</td>
<td>0.001 0.001</td>
<td>-0.006 0.004</td>
</tr>
<tr>
<td>N'-C'2, N'C'2</td>
<td>-0.002 0.001</td>
<td>-0.001 0.000</td>
<td>-0.003 0.001</td>
</tr>
<tr>
<td>C2-C3', C'6-C'6</td>
<td>-0.001 0.001</td>
<td>-0.001 -0.001</td>
<td>0.000 0.000</td>
</tr>
<tr>
<td>C1-C4', C'1-C'4</td>
<td>0.002 -0.002</td>
<td>0.000 0.000</td>
<td>-0.001 0.000</td>
</tr>
</tbody>
</table>

\(\alpha = \angle(\text{C}_6'-\text{C}_2',\text{C}_2-\text{C}_2)\)
\(\beta = \angle(\text{N'}-\text{Co}-\text{N}) = \angle(\text{N'}-\text{Co}-\text{N}')\)
\(\gamma = \angle(\text{N}^\prime-\text{C}_{2}^\prime-\text{C}_{2}-\text{N}) = \angle(\text{N}^\prime-\text{C}_{2}^\prime-\text{C}_{6}^\prime-\text{N})\)
\(\eta = d(\text{Co-N'/Co-N'})\)

\(\uparrow\)The \(D_{2d}\) and \(C_{2v}\) symmetry constraints impose that \(\beta' = 2\beta\) and \(\gamma = 0\).
Table 23 B3LYP/6-31G* 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).

<table>
<thead>
<tr>
<th>Parameters values in the C_{2v} geometries</th>
<th>^2A_1</th>
<th>D_{2d} \rightarrow C_{2v}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L_1</td>
<td>L_2</td>
</tr>
<tr>
<td>Co-N, Co-N''</td>
<td>2.027</td>
<td>2.225</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.889</td>
<td>1.966</td>
</tr>
<tr>
<td>N-C_2, N''-C_6''</td>
<td>1.362</td>
<td>1.349</td>
</tr>
<tr>
<td>N-C_6, N''-C_6''</td>
<td>1.339</td>
<td>1.335</td>
</tr>
<tr>
<td>C_2-C_3, C''_2-C_3'</td>
<td>1.389</td>
<td>1.390</td>
</tr>
<tr>
<td>C_2-C_4, C''_2-C_4'</td>
<td>1.390</td>
<td>1.390</td>
</tr>
<tr>
<td>C_2-C_6, C''_4-C_6'</td>
<td>1.389</td>
<td>1.390</td>
</tr>
<tr>
<td>C_2-C_6, C''_2-C_6'</td>
<td>1.390</td>
<td>1.390</td>
</tr>
<tr>
<td>C_2-C_3, C''_2-C_3'</td>
<td>1.471</td>
<td>1.483</td>
</tr>
<tr>
<td>N''-C_2, N'-C_6</td>
<td>1.350</td>
<td>1.354</td>
</tr>
<tr>
<td>C_2-C_3, C''_2-C_6'</td>
<td>1.393</td>
<td>1.395</td>
</tr>
<tr>
<td>C''_2,C''_4,C''_4,C''_5</td>
<td>1.392</td>
<td>1.388</td>
</tr>
<tr>
<td>\alpha = \angle(C''_6,C''_2,C''_2-C_3')</td>
<td>103.7</td>
<td>110.8</td>
</tr>
<tr>
<td>\beta = \angle(N''-Co-N) = \angle(N''-Co-N')</td>
<td>81.0</td>
<td>78.1</td>
</tr>
<tr>
<td>\beta' = \angle(N'-Co-N) \dagger</td>
<td>162.1</td>
<td>156.1</td>
</tr>
<tr>
<td>\gamma = \angle(N''-C''_2-C_3-N') = \angle(N''-C''_2-C_6-N') \dagger</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>\eta = \delta(Co-N'/Co-N'')</td>
<td>0.932</td>
<td>0.884</td>
</tr>
</tbody>
</table>

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

Table 24 B3LYP/6-31G* 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).

<table>
<thead>
<tr>
<th>Parameters values in the C_{2v} geometries</th>
<th>^2A_1</th>
<th>D_{2d} \rightarrow C_{2v}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L_1</td>
<td>L_2</td>
</tr>
<tr>
<td>Co-N, Co-N''</td>
<td>2.042</td>
<td>2.236</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.899</td>
<td>1.973</td>
</tr>
<tr>
<td>N-C_2, N''-C_6''</td>
<td>1.359</td>
<td>1.347</td>
</tr>
<tr>
<td>N-C_6, N''-C_6''</td>
<td>1.336</td>
<td>1.334</td>
</tr>
<tr>
<td>C_2-C_3, C''_2-C_3'</td>
<td>1.390</td>
<td>1.395</td>
</tr>
<tr>
<td>C_2-C_4, C''_2-C_4'</td>
<td>1.389</td>
<td>1.389</td>
</tr>
<tr>
<td>C_2-C_6, C''_4-C_6'</td>
<td>1.389</td>
<td>1.389</td>
</tr>
<tr>
<td>C_2-C_6, C''_2-C_6'</td>
<td>1.474</td>
<td>1.484</td>
</tr>
<tr>
<td>N''-C_2, N'-C_6</td>
<td>1.347</td>
<td>1.351</td>
</tr>
<tr>
<td>C_2-C_3, C''_2-C_3'</td>
<td>1.392</td>
<td>1.394</td>
</tr>
<tr>
<td>C_2-C_4, C''_2-C_4'</td>
<td>1.390</td>
<td>1.387</td>
</tr>
<tr>
<td>\alpha = \angle(C''_6,C''_2,C''_2-C_3')</td>
<td>104.2</td>
<td>111.1</td>
</tr>
<tr>
<td>\beta = \angle(N''-Co-N) = \angle(N''-Co-N')</td>
<td>80.8</td>
<td>77.9</td>
</tr>
<tr>
<td>\beta' = \angle(N'-Co-N) \dagger</td>
<td>161.6</td>
<td>155.8</td>
</tr>
<tr>
<td>\gamma = \angle(N''-C''_2-C_3-N') = \angle(N''-C''_2-C_6-N') \dagger</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>\eta = \delta(Co-N'/Co-N'')</td>
<td>0.930</td>
<td>0.882</td>
</tr>
</tbody>
</table>

\dagger The D_{2d} and C_{2v} symmetry constraints impose that \beta' = 2\beta and \gamma = 0.
**Table 25** HCTH407/6 – optimized LS [Co(tpy)₂]²⁺ geometry of C₂ᵥ symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the D₂d → C₂v symmetry lowering (²B₂ → ²A₁).

<table>
<thead>
<tr>
<th>Parameters values in the C₂ᵥ geometries</th>
<th>²A₁</th>
<th>²A₁</th>
<th>D₂d → C₂v</th>
<th>D₂d → C₂v</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>L₂</td>
<td>L₁</td>
<td>L₂</td>
<td>L₁</td>
</tr>
<tr>
<td>Co-N, Co-N'</td>
<td>2.013</td>
<td>2.220</td>
<td>-0.106</td>
<td>0.101</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.864</td>
<td>1.948</td>
<td>-0.025</td>
<td>0.059</td>
</tr>
<tr>
<td>N-C₂, N'-C'₂</td>
<td>1.361</td>
<td>1.347</td>
<td>0.008</td>
<td>-0.006</td>
</tr>
<tr>
<td>N-C₂, N'-C'₂</td>
<td>1.338</td>
<td>1.333</td>
<td>0.003</td>
<td>-0.002</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.392</td>
<td>1.397</td>
<td>-0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.387</td>
<td>1.388</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>C₂-C₆, C₂'-C₆'</td>
<td>1.388</td>
<td>1.388</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂-C₆, C₂'-C₆'</td>
<td>1.387</td>
<td>1.389</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>C₂-C₂', C₂'-C₂'</td>
<td>1.460</td>
<td>1.476</td>
<td>-0.007</td>
<td>0.009</td>
</tr>
<tr>
<td>N'-C₂, N'-C'₂</td>
<td>1.353</td>
<td>1.355</td>
<td>-0.003</td>
<td>-0.001</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.392</td>
<td>1.395</td>
<td>-0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>C₂-C₆, C₂'-C₆'</td>
<td>1.389</td>
<td>1.385</td>
<td>0.002</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

α = ∠(C₆-C₂, C₂-C₃)  
β = ∠(N'-Co-N) = ∠(N'-Co-N')  
β' = ∠(N'-Co-N)  
γ = ∠(N'-C₂-C₃-N) = ∠(N'-C₂'-C₆-N')  
η = d(Co-N'/Co-N')

The D₂d and C₂ᵥ symmetry constraints impose that β' = 2β and γ = 0.

**Table 26** OLYP/6 – optimized LS [Co(tpy)₂]²⁺ geometry of C₂ᵥ symmetry: selected bond lengths (Å) and angles (deg) and their variations upon the D₂d → C₂v symmetry lowering (²B₂ → ²A₁).

<table>
<thead>
<tr>
<th>Parameters values in the C₂ᵥ geometries</th>
<th>²A₁</th>
<th>²A₁</th>
<th>D₂d → C₂v</th>
<th>D₂d → C₂v</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁</td>
<td>L₂</td>
<td>L₁</td>
<td>L₂</td>
<td>L₁</td>
</tr>
<tr>
<td>Co-N, Co-N'</td>
<td>2.017</td>
<td>2.228</td>
<td>-0.108</td>
<td>0.103</td>
</tr>
<tr>
<td>Co-N'</td>
<td>1.869</td>
<td>1.956</td>
<td>-0.026</td>
<td>0.061</td>
</tr>
<tr>
<td>N-C₂, N'-C'₂</td>
<td>1.369</td>
<td>1.354</td>
<td>0.009</td>
<td>-0.006</td>
</tr>
<tr>
<td>N-C₂, N'-C'₂</td>
<td>1.346</td>
<td>1.340</td>
<td>0.003</td>
<td>-0.003</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.398</td>
<td>1.403</td>
<td>-0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.393</td>
<td>1.394</td>
<td>0.000</td>
<td>0.001</td>
</tr>
<tr>
<td>C₂-C₆, C₂'-C₆'</td>
<td>1.394</td>
<td>1.394</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂-C₆, C₂'-C₆'</td>
<td>1.393</td>
<td>1.394</td>
<td>-0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>C₂-C₂', C₂'-C₂'</td>
<td>1.466</td>
<td>1.482</td>
<td>-0.007</td>
<td>0.009</td>
</tr>
<tr>
<td>N'-C₂, N'-C'₂</td>
<td>1.360</td>
<td>1.362</td>
<td>-0.003</td>
<td>-0.001</td>
</tr>
<tr>
<td>C₂-C₃, C₂'-C₃'</td>
<td>1.398</td>
<td>1.400</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>C₂-C₆, C₂'-C₆'</td>
<td>1.395</td>
<td>1.391</td>
<td>0.002</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

α = ∠(C₆-C₂, C₂-C₃)  
β = ∠(N'-Co-N) = ∠(N'-Co-N')  
β' = ∠(N'-Co-N)  
γ = ∠(N'-C₂-C₃-N) = ∠(N'-C₂'-C₆-N')  
η = d(Co-N'/Co-N')

The D₂d and C₂ᵥ symmetry constraints impose that β' = 2β and γ = 0.
Table 27 PBE/γ –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 ($^{2}B_2 \rightarrow ^{2}A_1$).

<table>
<thead>
<tr>
<th>Parameters values in the $C_{2v}$ geometries</th>
<th>$^{2}A_1$</th>
<th>$D_{2d} \rightarrow C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L$_1$</td>
<td>L$_2$</td>
</tr>
<tr>
<td>Co-N, Co-N'$^\dagger$</td>
<td>1.982</td>
<td>2.186</td>
</tr>
<tr>
<td>Co-N$'$</td>
<td>1.845</td>
<td>1.927</td>
</tr>
<tr>
<td>N-C$_2$, N'$^\dagger$-C$_6'$</td>
<td>1.364</td>
<td>1.350</td>
</tr>
<tr>
<td>N-C$_8$, N'$^\dagger$-C$_6'$</td>
<td>1.342</td>
<td>1.337</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C'$^\dagger$-C$_3'$</td>
<td>1.395</td>
<td>1.399</td>
</tr>
<tr>
<td>C$_1$-C$_4$, C'$^\dagger$-C$_4'$</td>
<td>1.390</td>
<td>1.391</td>
</tr>
<tr>
<td>C$_1$-C$_5$, C'$^\dagger$-C$_5'$</td>
<td>1.392</td>
<td>1.392</td>
</tr>
<tr>
<td>C$_3$-C$_6$, C'$^\dagger$-C$_3'$</td>
<td>1.390</td>
<td>1.392</td>
</tr>
<tr>
<td>C$_2$-C$_2'$, C$_5$-C$_6'$</td>
<td>1.460</td>
<td>1.475</td>
</tr>
<tr>
<td>N'$^\dagger$-C$_2$, N'-C$_6'$</td>
<td>1.356</td>
<td>1.357</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_4$-C$_6'$</td>
<td>1.395</td>
<td>1.397</td>
</tr>
<tr>
<td>C'$^\dagger$-C$_4$, C$_3$-C$_5$</td>
<td>1.392</td>
<td>1.389</td>
</tr>
<tr>
<td>$\alpha$ = $\angle$ (C$_6$-C$_2$, C$_2$-C$_3'$)</td>
<td>103.0</td>
<td>110.2</td>
</tr>
<tr>
<td>$\beta$ = $\angle$ (N$'$-Co-N) = $\angle$ (N'$^\dagger$-Co-N')</td>
<td>81.6</td>
<td>78.7</td>
</tr>
<tr>
<td>$\beta'$ = $\angle$ (N$'$-Co-N')$^\dagger$</td>
<td>163.3</td>
<td>157.3</td>
</tr>
<tr>
<td>$\gamma$ = $\angle$ (N$'$-C$_2$-C$_3$-N) = $\angle$ (N$'$-C$_2$'-C$_6$-N')$^\dagger$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta$ = d(Co-N'(Co-N$'$))</td>
<td>0.931</td>
<td>0.882</td>
</tr>
</tbody>
</table>

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

Table 28 PBE/γ –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 ($^{2}B_2 \rightarrow ^{2}A_1$).

<table>
<thead>
<tr>
<th>Parameters values in the $C_{2v}$ geometries</th>
<th>$^{2}A_1$</th>
<th>$D_{2d} \rightarrow C_{2v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L$_1$</td>
<td>L$_2$</td>
</tr>
<tr>
<td>Co-N, Co-N'$^\dagger$</td>
<td>1.988</td>
<td>2.186</td>
</tr>
<tr>
<td>Co-N$'$</td>
<td>1.863</td>
<td>1.944</td>
</tr>
<tr>
<td>N-C$_2$, N'$^\dagger$-C$_6'$</td>
<td>1.372</td>
<td>1.357</td>
</tr>
<tr>
<td>N-C$_8$, N'$^\dagger$-C$_6'$</td>
<td>1.347</td>
<td>1.342</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C'$^\dagger$-C$_3'$</td>
<td>1.397</td>
<td>1.401</td>
</tr>
<tr>
<td>C$_1$-C$_4$, C'$^\dagger$-C$_4'$</td>
<td>1.394</td>
<td>1.395</td>
</tr>
<tr>
<td>C$_1$-C$_5$, C'$^\dagger$-C$_5'$</td>
<td>1.396</td>
<td>1.396</td>
</tr>
<tr>
<td>C$_3$-C$_6$, C'$^\dagger$-C$_3'$</td>
<td>1.394</td>
<td>1.395</td>
</tr>
<tr>
<td>C$_2$-C$_2'$, C$_5$-C$_6'$</td>
<td>1.464</td>
<td>1.478</td>
</tr>
<tr>
<td>N'$^\dagger$-C$_2$, N'-C$_6'$</td>
<td>1.362</td>
<td>1.362</td>
</tr>
<tr>
<td>C$_2$-C$_3$, C$_4$-C$_6'$</td>
<td>1.398</td>
<td>1.400</td>
</tr>
<tr>
<td>C'$^\dagger$-C$_4$, C$_3$-C$_5$</td>
<td>1.397</td>
<td>1.394</td>
</tr>
<tr>
<td>$\alpha$ = $\angle$ (C$_6$-C$_2$, C$_2$-C$_3'$)</td>
<td>102.7</td>
<td>109.7</td>
</tr>
<tr>
<td>$\beta$ = $\angle$ (N$'$-Co-N) = $\angle$ (N'$^\dagger$-Co-N')</td>
<td>81.6</td>
<td>78.6</td>
</tr>
<tr>
<td>$\beta'$ = $\angle$ (N$'$-Co-N')$^\dagger$</td>
<td>163.1</td>
<td>157.1</td>
</tr>
<tr>
<td>$\gamma$ = $\angle$ (N$'$-C$_2$-C$_3$-N) = $\angle$ (N$'$-C$_2$'-C$_6$-N')$^\dagger$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\eta$ = d(Co-N'(Co-N$'$))</td>
<td>0.937</td>
<td>0.889</td>
</tr>
</tbody>
</table>

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

25
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).

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic results</th>
<th></th>
<th>Scalar relativistic results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LS $^4$B$_2$</td>
<td>HS $^4$A$_2$</td>
<td>LS $^4$B$_2$</td>
</tr>
<tr>
<td></td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
<td>L$_1$, L$_2$</td>
</tr>
<tr>
<td></td>
<td>$^4$E</td>
<td></td>
<td>$^4$A$_2$</td>
</tr>
<tr>
<td></td>
<td>L$_1$, L$_2$</td>
<td></td>
<td>L$_1$, L$_2$</td>
</tr>
<tr>
<td>Co-N, Co-N$''$</td>
<td>2.118</td>
<td>2.188</td>
<td>2.188</td>
</tr>
<tr>
<td>Co-N$'$</td>
<td>1.891</td>
<td>2.057</td>
<td>2.060</td>
</tr>
<tr>
<td>$\alpha = \angle$(C$_6$-C$_2''$, C$_2$-C$_2''$)</td>
<td>107.7</td>
<td>108.0</td>
<td>108.2</td>
</tr>
<tr>
<td>$\beta = \angle$(N'-Co-N) = $\angle$(N''-Co-N')</td>
<td>80.1</td>
<td>76.5</td>
<td>76.3</td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic results</th>
<th></th>
<th>Scalar relativistic results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LS $^4$A$_1$</td>
<td>HS $^4$A$_2$</td>
<td>LS $^4$B$_1$</td>
</tr>
<tr>
<td></td>
<td>L$_1$</td>
<td>L$_2$</td>
<td>L$_1$</td>
</tr>
<tr>
<td></td>
<td>L$_2$</td>
<td></td>
<td>L$_1$, L$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^4$B$_1$</td>
</tr>
<tr>
<td>Co-N, Co-N$''$</td>
<td>2.020</td>
<td>2.221</td>
<td>2.195</td>
</tr>
<tr>
<td>Co-N$'$</td>
<td>1.870</td>
<td>1.956</td>
<td>2.059</td>
</tr>
<tr>
<td>$\alpha = \angle$(C$_N$-C$_2''$, C$_2$-C$_2''$)</td>
<td>104.0</td>
<td>111.0</td>
<td>108.3</td>
</tr>
<tr>
<td>$\beta = \angle$(N'-Co-N) = $\angle$(N''-Co-N')</td>
<td>81.1</td>
<td>78.0</td>
<td>76.4</td>
</tr>
</tbody>
</table>

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

![Atom labelling used for $[\text{Co(bpy)}_3]^{2+}$](image)

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

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Scalar relativistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N = Co-N'</td>
<td>2.179</td>
<td>2.169</td>
</tr>
<tr>
<td>$\beta = \angle(N'-\text{Co-N})$</td>
<td>75.6</td>
<td>75.8</td>
</tr>
<tr>
<td>$\gamma = \angle(N'-C'_2-C_2-N)$</td>
<td>6.1</td>
<td>6.8</td>
</tr>
</tbody>
</table>

**Table 32** Influence of scalar relativistic effects on the optimized $C_2$ geometry of $[\text{Co(bpy)}_3]^{2+}$ 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.

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Scalar relativistic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ligand L1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N = Co-N'</td>
<td>1.973</td>
<td>1.962</td>
</tr>
<tr>
<td>$\beta = \angle(N'-\text{Co-N})$</td>
<td>81.6</td>
<td>81.9</td>
</tr>
<tr>
<td>$\gamma = \angle(N'-C'_2-C_2-N)$</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>Ligands L2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N</td>
<td>2.002</td>
<td>1.991</td>
</tr>
<tr>
<td>Co-N'</td>
<td>2.250</td>
<td>2.244</td>
</tr>
<tr>
<td>$\beta = \angle(N'-\text{Co-N})$</td>
<td>77.6</td>
<td>77.8</td>
</tr>
<tr>
<td>$\gamma = \angle(N'-C'_2-C_2-N)$</td>
<td>13.3</td>
<td>13.6</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th></th>
<th>LS</th>
<th>HS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L1, L2, L3</td>
<td>L1, L2, L3</td>
</tr>
<tr>
<td><strong>Non relativistic results</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N</td>
<td>2.303 1.908</td>
<td>2.151 2.148</td>
</tr>
<tr>
<td>N-C</td>
<td>1.154 1.151</td>
<td>1.153 1.153</td>
</tr>
<tr>
<td>C-H</td>
<td>1.077 1.077</td>
<td>1.077 1.078</td>
</tr>
<tr>
<td><strong>Scalar relativistic results</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-N</td>
<td>2.299 1.896</td>
<td>2.138 2.138</td>
</tr>
<tr>
<td>N-C</td>
<td>1.154 1.151</td>
<td>1.153 1.152</td>
</tr>
<tr>
<td>C-H</td>
<td>1.077 1.077</td>
<td>1.077 1.078</td>
</tr>
</tbody>
</table>

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 (\(\Delta \text{E}_{\text{HL}}\)) and its electronic (\(\Delta \text{E}_{\text{HL}}^{\text{el}}\)) and vibrational (\(\Delta \text{E}_{\text{HL}}^{\text{vib}}\)) components. For [Co(tpy)\(_2\)]\(^{2+}\), the scalar relativistic shifts to the pseudo-Jahn-Teller stabilization energy in the LS state (\(E_{\text{PJT}}\)), to the tetragonal splitting of the HS in \(D_{2d}\) (\(\Delta_{\text{HS}}\)) and in \(C_{2v}\) (\(\Delta_{\text{HS}}'\)) are also given.

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Scalar relativistic</th>
<th>Scalar relativistic shift</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The [Co(tpy)(_2)](^{2+}) complex</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}})</td>
<td>3160</td>
<td>3546</td>
<td>+386</td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}}^{\text{el}})</td>
<td>−180</td>
<td>−219</td>
<td>−39</td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}}^{\text{vib}})</td>
<td>2980</td>
<td>3326</td>
<td>+347</td>
</tr>
<tr>
<td>(E_{\text{PJT}})</td>
<td>204</td>
<td>221</td>
<td>+17</td>
</tr>
<tr>
<td>(\Delta_{\text{HS}})</td>
<td>423</td>
<td>474</td>
<td>+51</td>
</tr>
<tr>
<td>(\Delta_{\text{HS}}')</td>
<td>−288</td>
<td>−216</td>
<td>+72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Scalar relativistic</th>
<th>Scalar relativistic shift</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The [Co(bpy)(_3)](^{2+}) complex</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}})</td>
<td>394</td>
<td>668</td>
<td>+274</td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}}^{\text{el}})</td>
<td>−309</td>
<td>−330</td>
<td>−21</td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}}^{\text{vib}})</td>
<td>85</td>
<td>338</td>
<td>253</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Nonrelativistic</th>
<th>Scalar relativistic</th>
<th>Scalar relativistic shift</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>The [Co(NCH)(_6)](^{2+}) complex</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}})</td>
<td>−809</td>
<td>−192</td>
<td>+617</td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}}^{\text{el}})</td>
<td>−484</td>
<td>−504</td>
<td>−20</td>
</tr>
<tr>
<td>(\Delta \text{E}_{\text{HL}}^{\text{vib}})</td>
<td>−1293</td>
<td>−696</td>
<td>+597</td>
</tr>
</tbody>
</table>