Theoretical investigation on the ground state properties of the hexaamminecobalt(III) and nitro-nitrito linkage isomerism in pentaamminecobalt(III) \textit{in vacuo}

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Electronic supplementary information

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Figure S1. Selected valence molecular orbitals of $D_{5h} [\text{Co(NH}_3)_6]^{3+}$ computed at wB97XD/6-31+G(d,p)
**Figure S2.** Optimized geometries of D$_{3d}$ (a) and D$_3$ (b) at wB97XD/6-31+G(d,p)

**Figure S3.** (a) Equilibrium geometry of Co(NH$_3$)$_6^{3+}$ in D$_{3d}$ symmetry, (b) distortion vector from D$_{3d}$ to D$_3$, and imaginary vibrational modes of a$_{2g}$ (c), a$_{1u}$ (d), e$_g$ (e) and e$_u$ (f) symmetry
Figure S4. Imaginary vibrational modes of TS1-3

Figure S5. Intrinsic reaction coordinates plot of the intramolecular conversion between nitro isomer and endo-nitrito intermediate via TS1 computed at wB97XD/6-31+G(d,p)
Table S1. Energies of valence molecular orbitals in Hartrees of D\textsubscript{3} and D\textsubscript{3d}\textsuperscript{−}[Co(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+} computed at B3LYP/TZVP

| D\textsubscript{3d} | Energies | D\textsubscript{3} | Energies |
|---------------------|----------|---------------------|----------|
| 6a\textsubscript{2u} | -0.8392  | 12e                 | -0.8355  |
| 7e\textsubscript{u}  | -0.8345  | 7a\textsubscript{2}  | -0.8354  |
| 8a\textsubscript{1g} | -0.8007  | 9a\textsubscript{1}  | -0.7992  |
| 6e\textsubscript{g}  | -0.7998  | 13e                 | -0.7988  |
| 7e\textsubscript{g}  | -0.5700  | 14e                 | -0.5690  |
| 9a\textsubscript{1g} | -0.4585  | 10a\textsubscript{1} | -0.4572  |
| 7a\textsubscript{2u} | -0.4091  | 15e                 | -0.4049  |
| 8e\textsubscript{u}  | -0.4039  | 8a\textsubscript{2}  | -0.4039  |

The HOMO is in italic

Table S2. Relative energies of the D\textsubscript{3}, S\textsubscript{6} and C\textsubscript{2h} epikernels with respect to D\textsubscript{3} geometries computed at B3LYP, ωB97XD and OPBE with ccpVtz.

|       | B3LYP | ωB97XD | OPBE |
|-------|-------|--------|------|
| D\textsubscript{3} | -1.52 | -1.78  | -1.64 |
| S\textsubscript{6}  | -1.18 | -1.35  | -1.24 |
| C\textsubscript{2h} | -1.16 | -1.32  | -1.21 |
Table S3. Imaginary frequencies of [Co(NH)_3]_6^{3+} in D_{3d} and C_{2h} and its lowest real frequencies of D3 and S6 geometries computed at B3LYP, \(ωB97XD\) and OPBE with ccPVTZ.

|          | B3LYP          | \(ωB97XD\)     | OPBE          |
|----------|----------------|----------------|---------------|
| D_{3d}   | i_{132}(a1u)+i_{128}(a2g) | i_{145}(a1u)+i_{141}(a2g) | i_{135}(a1u)+i_{131}(a2g) |
|          | +i_{55}(eg)+i_{19}(eu)      | +i_{69}(eg)+i_{33}(eu)      | +i_{49}(eg)     |
| D_{3}    | 80 (e)          | 81 (e)         | 84 (e)        |
| S_{6}    | 40 (eu)         | 49 (eu)        | 42 (eu)       |
| C_{2h}   | i_{61}(au)+i_{40}(bg)   | i_{58}(au)+i_{30}(bg)      | i_{65}(au)+i_{38}(bg) |

Table S4. Comparison of bond lengths and angles between X-ray structure and calculated geometries of Co-NO2, exo-Co-ONO, endo-Co-ONO and TS complexes computed at \(ωB97XD/6-31+G(d,p)\) and B3LYP/LanL2DZ[] (values of bond lengths in Å and angles in degrees).

| parameters | nitro | nitrito | Endo- | TS1   |
|------------|-------|--------|-------|-------|
|            | This work | Ciofini work\[^{78}\] | Exp[^{79}\] | This work | Ciofini work\[^{78}\] | Exp[^{80}\] | This work | This work | Ciofini work\[^{78}\] |
| Co-N1      | 1.924 | 1.973 | 1.921 | 2.776 | 2.875 | 2.930 | 2.269 | 2.382 |
| Co-N2      | 1.997 | 2.020 | 1.978 | 1.993 | 2.014 | 1.913 | 1.992 | 2.008 | 2.006 |
| Co-N3      | 2.064 | 2.062 | 1.976 | 2.024 | 2.029 | 1.948 | 2.031 | 1.979 | 2.031 |
| Co-N4      | 1.995 | 2.019 | 1.978 | 1.993 | 2.013 | 1.968 | 1.998 | 1.997 | 2.033 |
| Co-N5      | 1.999 | 2.021 | 1.978 | 1.997 | 2.012 | 1.952 | 1.999 | 1.977 | 2.005 |
| Co-N6      | 1.997 | 2.019 | 1.978 | 1.988 | 2.015 | 1.954 | 1.990 | 1.994 | 2.004 |
| Co-O2      | 2.719 | 2.804 | -     | 1.858 | 1.893 | 1.927 | 1.891 | 2.346 | 2.409 |
| N1-O2      | 1.221 | 1.272 | 1.161 | 1.381 | 1.463 | 1.244 | 1.318 | 1.272 | 1.344 |
Table S5. Relative energies (RE in kcal/mol) of different isomers and transition states, HOMO-LUMO gap energies (H-L in eV) of Co-NO$_2$ and Co-ONO computed using different methods at 6-31+G(d,p). TS1 and TS2 are transition states

| Methods          | RE(exo) | RE(endo) | RE(TS1) | RE(TS2) | H-L  |
|------------------|---------|----------|---------|---------|------|
| CCSD(T)(a)       | 2.00    | 1.12     | 43.78   | 10.76   | 13.64|
| MP2              | 3.98    | 4.81     | 40.90   | 12.59   | 12.95|
| B3LYP            | 4.43    | 2.25     | 40.73   | 13.40   | 4.46 |
| B3LYP-D3         | 4.42    | 1.83     | -       | 5.64    | 4.52 |
| M062X            | -0.53   | -2.77    | 36.76   | 7.00    | 7.65 |
| wB97XD           | 3.39    | 1.32     | 40.89   | 12.70   | 8.68 |

(a) CCSD(T)/6-31G(d) single point calculation from MP2/6-31+G(d,p) optimized geometry

[78] I. Ciofini, C. Adamo, JPHYSChemA 2001, 105, 1086-1092
[79] F.A Cotton, W.T Edwards, Acta Crystallogr. B 1968, 24, 474
[80] I. Grenthe, E. Nordin, Inorg. Chem. 1979, 18, 1869
### Table S6. Energies of valence orbitals in Hartrees of the nitro/nitrito linkage isomers computed at wB97XD/6-31+G(d,p)

| Orbitals | Co-NO$_2$ | exo-Co-ONO | endo-Co-ONO |
|----------|-----------|------------|-------------|
| L+3      | -0.24467  | -0.24246   | -0.24311    |
| L+2      | -0.26644  | -0.24388   | -0.25377    |
| L+1      | -0.31722  | -0.30936   | -0.31871    |
| L        | -0.31968  | -0.31741   | -0.31964    |
| H        | -0.63876  | -0.59813   | -0.61054    |
| H-1      | -0.66656  | -0.65652   | -0.67549    |
| H-2      | -0.67931  | -0.68464   | -0.68020    |
| H-3      | -0.72491  | -0.72708   | -0.72869    |
| H-4      | -0.72828  | -0.72858   | -0.73044    |
| H-5      | -0.73013  | -0.73434   | -0.73698    |
| H-6      | -0.76630  | -0.76118   | -0.76295    |

The HOMO (H) and LUMO (L) are in italic.

### Table S7. Topological properties of the electron density of Co-NO$_2$ and Co-ONO: electron densities and their Laplacian in parenthesis at different bond critical points in Co-complexes computed at wB97XD/6-31+G(d,p).

| Bonds     | Co-NO$_2$         | Exo-Co-ONO | Endo-Co-ONO |
|-----------|-------------------|------------|-------------|
| Co-NH$_3$ | 0.088(-0.108)     | 0.090(-0.109) | 0.090(-0.107) |
| Co-N     | 0.118(-0.106)     | -          | -           |
| Co-O     | -                 | 0.116(-0.154) | 0.104(-0.136) |
| ON-O     | 0.501(0.263)      | 0.561(0.392) | 0.523(0.339) |
| (Co)O-N  | 0.499(0.261)      | 0.340(0.102) | 0.399(0.163) |
| N-H      | 0.331(0.448)      | 0.329(0.445) | 0.331(0.448) |
| N…H     | 0.022(-0.018)     | -          | -           |
| NO…H    | 0.019(-0.018)     | -          | 0.022(-0.017) |
| O…N     | -                 | -          |             |
Gaussian09 outputs of D$_3$ and D$_{3d}$-Co(NH$_3$)$_6^{3+}$ calculations at CCSD(T) and BD(T) levels

(Enter /usr/local/gaussian/g09D01/g09/19999.exe)

1\:\:GINC-QUANTUM33\:SP\:RCCSD(T)\:FC\:6-31+G(d,p)\:Co1H18N6(3+)\:JMUYA\:09-Ma

y-2016/0\:Gp\:ccsd-t-6-31+G(d,p)\:symm=loose\:title\:3,1\:Co,0,0,0,0,0,0

,0,1,390677702,0,85644291,-1,156462665,N,0,0,0463642666,-1,632583673,-1 ,1,56462665,N,0,-1,437040168,0,776140763,-1,156462665,N,0,-1,437040168, ,0,776140763,1,156462665,N,0,0,0463642666,1,632583673,1,156462665,N,0,1 ,390677702,-0,85644291,1,156462665,H,0,1,52323731,0,418728808,-2,07316 ,8164,H,0,1,19998338,1,836474168,-1,378596498,H,0,2,334081969,0,887612 ,993,-0,758916332,H,0,-0,39898887,-1,528526611,-2,073168164,H,0,0,99493 ,4114,-1,9496719,-1,378596498,H,0,-0,398345583,2,465180776,-0,75891633 ,2,185932451,0,113197732,-1,378596498,H,0,-1,935736385,1,5775677 ,83,-0,758916332,H,0,-1,12424844,1,109797802,-2,073168164,H,0,-1,935736 ,385,-1,577567783,0,758916332,H,0,-1,12424844,-1,109797802,2,073168164,H, ,0,1,185932451,-0,113197732,1,378596498,H,0,-0,398345583,2,465180776 ,0,758916332,H,0,-0,39898887,1,528526611,2,073168164,H,0,0,994934114,1 ,9496719,1,378596498,H,0,1,19998338,1,836474168,1,378596498,H,0,2,33 ,4081969,-0,887612993,0,758916332,H,0,1,52323731,-0,418728808,2,0731681 ,64\:Version=ES64L-G09RevD.01\:State=1-A1\:HF=-1717.4954481\:MP2=-1718.888 \:0972\:MP3=-1718.9601737\:MP4D=-1718.9601737\:MP4DQ=-1718.9808716\:CCSD=-1718.9834351\:CCSD(T)=1719.0362302\:RMSD=2.646e-09\:P 

G=D03 [O(Con1),X(H18N6)]

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412024,-1.818023563,1.068027\H,0,1.533412024,-1.818023563,1.068027\H,0
,2.341160602,-0.418961986,1.068027\H,0,1.221812944,-0.705414032,2.1845
36\H,0,-0.807748578,-2.236985549,-1.068027\H,0,-1.4010828064,-2.1845
36\H,0,0.807748578,-2.236985549,-1.068027\H,0,2.341160602,0.418961986,
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1718.918593\MP4D=--1718.9566107\MP4DQ=--1718.9381087\MP4SDQ=--1718.97730
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1),3SGD(H2N2),X(H12)]\@

UPON JULIA'S CLOTHES

WHENAS IN SILKS MY JULIA GOES,
THEN, THEN, METHINKS, HOW SWEETLY FLOWS
THAT LIQUEFACTION OF HER CLOTHES.
NEXT, WHEN I CAST MINE EYES, AND SEE
THAT BRAVE VIBRATION, EACH WAY FREE,
O, HOW THAT GLITTERING TAKETH ME!

-- ROBERT HERRICK, 1648

Job cpu time: 0 days 3 hours 51 minutes 46.2 seconds.
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THEORY: SUPPOSITION WHICH HAS SCIENTIFIC BASIS, BUT NOT EXPERIMENTALLY PROVEN.

FACT: A THEORY WHICH HAS BEEN PROVEN BY ENOUGH MONEY TO PAY FOR THE EXPERIMENTS.

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,0.758916332\H,0,-0.39898887,1.528526611,2.073168164\H,0,0.99493411
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GARBAGE IN, GARBAGE OUT

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