# The Lanthanide Contraction Revisited

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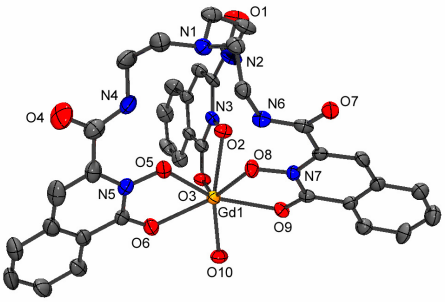
# 1. TREN-1,2-HOIQO Lanthanide Complexes

## 1.1 Structure




Asymmetric unit of [Gd(TREN-1,2-HOIQO)($H_2O$)]*$H_2O$. Thermal ellipsoid plot (Ortep 3 for Windows,[1] 50% probability level) with atom numbering scheme. Hydrogens and the isolated water molecule omitted for clarity.

## 1.2 Bond Lengths

Table S1. Bond lengths in [Ln(TREN-1,2-HOIQO)($H_2O$)]*$H_2O$.

| f electrons (Ln) | $d_{Ln-O3}$ (su) [Å] | $d_{Ln-O6}$ (su) [Å] | $d_{Ln-O9}$ (su) [Å] | $d_{Ln-O2}$ (su) [Å] | $d_{Ln-O5}$ (su) [Å] | $d_{Ln-O8}$ (su) [Å] | $d_{Ln-O10}$ (su) [Å] | $d_{Ln-O7}$ (su) [Å] | $\Sigma d_{Ln-O}$ (su) [Å] |
|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | 2.482(4) | 2.463(4) | 2.479(4) | 2.447(4) | 2.443(5) | 2.473(4) | 2.581(4) | 2.516(4) | 19.884(34) |
| 1 (Ce)[2] | 2.469(4) | 2.445(4) | 2.450(4) | 2.432(4) | 2.426(4) | 2.445(4) | 2.573(4) | 2.478(4) | 19.718(32) |
| 2 (Pr) | 2.452(4) | 2.427(4) | 2.428(4) | 2.407(4) | 2.405(4) | 2.437(3) | 2.556(4) | 2.473(4) | 19.585(31) |
| 3 (Nd) | 2.434(4) | 2.397(4) | 2.415(4) | 2.395(4) | 2.394(4) | 2.418(4) | 2.536(4) | 2.461(4) | 19.450(32) |
| 4 (Pm) | - | - | - | - | - | - | - | - | - |
| 5 (Sm) | 2.396(4) | 2.381(4) | 2.374(4) | 2.377(4) | 2.377(4) | 2.396(4) | 2.518(4) | 2.434(4) | 19.253(32) |
| 6 (Eu) | 2.384(5) | 2.368(5) | 2.356(5) | 2.361(5) | 2.367(5) | 2.386(5) | 2.501(5) | 2.420(5) | 19.143(40) |
| 7 (Gd) | 2.373(5) | 2.357(5) | 2.349(5) | 2.352(4) | 2.343(5) | 2.376(4) | 2.491(5) | 2.403(5) | 19.044(38) |
| 8 (Tb) | 2.356(4) | 2.338(4) | 2.333(4) | 2.336(4) | 2.332(4) | 2.361(4) | 2.462(4) | 2.381(4) | 18.899(32) |
| 9 (Dy) | 2.340(4) | 2.335(4) | 2.322(4) | 2.329(4) | 2.327(4) | 2.355(4) | 2.460(4) | 2.375(4) | 18.843(32) |
| 10 (Ho) | 2.327(5) | 2.318(5) | 2.313(5) | 2.312(5) | 2.311(5) | 2.333(5) | 2.456(5) | 2.353(5) | 18.723(40) |
| 11 (Er) | 2.314(4) | 2.309(5) | 2.307(4) | 2.307(4) | 2.313(4) | 2.330(4) | 2.442(5) | 2.353(4) | 18.675(34) |
| 12 (Tm) | 2.308(4) | 2.300(4) | 2.294(4) | 2.297(4) | 2.304(4) | 2.324(4) | 2.424(4) | 2.338(4) | 18.589(32) |
| 13 (Yb) | 2.277(6) | 2.282(6) | 2.265(6) | 2.300(6) | 2.286(6) | 2.301(6) | 2.437(6) | 2.333(6) | 18.481(48) |
| 14(Lu) | 2.288(3) | 2.292(3) | 2.282(3) | 2.294(3) | 2.287(3) | 2.320(3) | 2.418(3) | 2.329(3) | 18.510(24) |
| $d_{La}$ / $d_{Lu}$ | 1.085 | 1.075 | 1.086 | 1.067 | 1.068 | 1.066 | 1.067 | 1.080 | 1.074 |

## 1.3 O-O Distances

Table S2. Distances O-O (O bound to Ln) in [Ln(TREN-1,2-HOIQO)($H_2O$)]*$H_2O$.

| f electrons (Ln) | $d_{O7-O9}$ [Å] | $d_{O3-O5}$ [Å] | $d_{O7-O5}$ [Å] | $d_{O3-O9}$ [Å] | $d_{O5-O6}$ [Å] | $d_{O9-O10}$ [Å] | $d_{O2-O3}$ [Å] | $d_{O7-O8}$ [Å] | $d_{O7-O10}$ [Å] | $d_{O3-O6}$ [Å] | $d_{O7-O6}$ [Å] | $d_{O10-O3}$ [Å] | $d_{O2-O5}$ [Å] | $d_{O2-O9}$ [Å] | $d_{O9-O8}$ [Å] | $d_{O8-O5}$ [Å] | $d_{O6-O10}$ [Å] | $d_{O2-O8}$ [Å] | $\Sigma d_{O-O}$ [Å] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | 3.120 | 3.942 | 3.408 | 3.960 | 2.568 | 3.213 | 2.557 | 3.078 | 3.124 | 3.284 | 3.143 | 3.092 | 3.158 | 3.602 | 2.576 | 3.090 | 2.905 | 2.915 | 56.735 |
| 1 (Ce)[2] | 3.109 | 3.902 | 3.379 | 3.912 | 2.555 | 3.159 | 2.562 | 3.043 | 3.104 | 3.224 | 3.122 | 3.064 | 3.128 | 3.555 | 2.574 | 3.065 | 2.907 | 2.881 | 56.245 |
| 2 (Pr) | 3.112 | 3.908 | 3.353 | 3.840 | 2.557 | 3.119 | 2.551 | 3.039 | 3.086 | 3.217 | 3.100 | 3.023 | 3.106 | 3.509 | 2.576 | 3.031 | 2.884 | 2.862 | 55.873 |
| 3 (Nd) | 3.112 | 3.897 | 3.335 | 3.793 | 2.551 | 3.086 | 2.549 | 3.006 | 3.072 | 3.190 | 3.077 | 2.992 | 3.086 | 3.477 | 2.576 | 2.997 | 2.856 | 2.843 | 55.495 |
| 4 (Pm) | - | - | - | - | - | - | | | | | | | | | | | | | |
| 5 (Sm) | 3.085 | 3.865 | 3.319 | 3.703 | 2.562 | 3.023 | 2.567 | 2.986 | 3.040 | 3.135 | 3.054 | 2.931 | 3.040 | 3.428 | 2.573 | 2.959 | 2.839 | 2.795 | 54.904 |
| 6 (Eu) | 3.083 | 3.866 | 3.294 | 3.646 | 2.560 | 2.976 | 2.551 | 2.967 | 3.031 | 3.137 | 3.038 | 2.910 | 3.023 | 3.392 | 2.570 | 2.940 | 2.838 | 2.775 | 54.597 |
| 7 (Gd) | 3.085 | 3.852 | 3.258 | 3.610 | 2.562 | 2.973 | 2.546 | 2.953 | 3.015 | 3.120 | 3.023 | 2.888 | 3.012 | 3.363 | 2.565 | 2.914 | 2.804 | 2.758 | 54.301 |
| 8 (Tb) | 3.067 | 3.823 | 3.253 | 3.578 | 2.556 | 2.936 | 2.534 | 2.928 | 2.976 | 3.074 | 3.004 | 2.850 | 2.995 | 3.326 | 2.567 | 2.890 | 2.774 | 2.749 | 53.880 |
| 9 (Dy) | 3.074 | 3.817 | 3.237 | 3.535 | 2.558 | 2.901 | 2.544 | 2.918 | 2.969 | 3.063 | 3.001 | 2.842 | 2.984 | 3.302 | 2.570 | 2.881 | 2.788 | 2.724 | 53.708 |
| 10 (Ho) | 3.061 | 3.795 | 3.208 | 3.515 | 2.552 | 2.891 | 2.539 | 2.884 | 2.959 | 3.033 | 2.977 | 2.826 | 2.955 | 3.284 | 2.558 | 2.855 | 2.767 | 2.702 | 53.361 |
| 11 (Er) | 3.060 | 3.792 | 3.211 | 3.489 | 2.544 | 2.876 | 2.549 | 2.884 | 2.948 | 3.018 | 2.976 | 2.802 | 2.953 | 3.272 | 2.564 | 2.853 | 2.753 | 2.684 | 53.228 |
| 12 (Tm) | 3.059 | 3.775 | 3.217 | 3.470 | 2.562 | 2.854 | 2.538 | 2.881 | 2.924 | 2.998 | 2.966 | 2.792 | 2.933 | 3.248 | 2.572 | 2.835 | 2.736 | 2.682 | 53.042 |
| 13 (Yb) | 3.042 | 3.738 | 3.188 | 3.412 | 2.542 | 2.824 | 2.521 | 2.856 | 2.920 | 2.958 | 2.954 | 2.788 | 2.927 | 3.221 | 2.544 | 2.809 | 2.741 | 2.669 | 52.654 |
| 14 (Lu) | 3.054 | 3.752 | 3.194 | 3.417 | 2.552 | 2.831 | 2.535 | 2.860 | 2.913 | 2.974 | 2.956 | 2.761 | 2.928 | 3.216 | 2.579 | 2.812 | 2.722 | 2.674 | 52.730 |
| $d_{La}$ / $d_{Lu}$ | 1.022 | 1.051 | 1.067 | 1.159 | 1.006 | 1.135 | 1.009 | 1.076 | 1.072 | 1.104 | 1.063 | 1.120 | 1.079 | 1.120 | 0.999 | 1.090 | 1.067 | 1.090 | 1.076 |

## 1.4 Dihedral Angles along the Edges of the Coordination Polyhedron

Table S3. Dihedral angles along the edges of the coordination polyhedron [°]. Shape measure $SM_{tdh}$ (deviation relative to an ideal trigonal-dodecahedron) and $SM_{Gd}$ (deviation relative to the gadolinium complex).[3]

| edge | ideal | La | Ce[2] | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O7-O8 | 74.3 | 55.07 | 55.68 | 56.25 | 56.68 | 57.31 | 57.75 | 57.94 | 58.37 | 58.77 | 58.70 | 58.85 | 59.35 | 59.72 | 60.10 |
| O7-O5 | 29.9 | 41.41 | 41.56 | 41.77 | 42.10 | 42.00 | 42.24 | 42.42 | 42.09 | 42.36 | 42.54 | 42.75 | 42.31 | 43.00 | 41.60 |
| O7-O6 | 61.5 | 49.04 | 48.85 | 49.16 | 49.02 | 49.25 | 49.54 | 49.40 | 49.45 | 49.51 | 49.18 | 49.02 | 49.47 | 48.91 | 50.19 |
| O7-O10 | 61.5 | 56.74 | 57.09 | 57.40 | 57.55 | 57.88 | 57.89 | 57.86 | 57.90 | 58.21 | 58.17 | 58.30 | 58.38 | 59.55 | 57.81 |
| O7-O9 | 29.9 | 47.45 | 46.36 | 45.77 | 45.51 | 44.62 | 43.87 | 43.60 | 43.44 | 42.49 | 42.23 | 42.41 | 42.03 | 40.98 | 41.47 |
| O6-O10 | 53.2 | 61.63 | 61.31 | 61.04 | 60.82 | 60.79 | 60.78 | 61.22 | 60.70 | 60.74 | 60.98 | 60.80 | 60.54 | 60.87 | 61.31 |
| O9-O10 | 74.3 | 68.17 | 69.12 | 68.39 | 68.26 | 68.38 | 68.31 | 68.07 | 67.95 | 68.35 | 68.79 | 68.42 | 68.37 | 69.03 | 68.33 |
| O3-O9 | 29.9 | 30.36 | 29.78 | 30.81 | 31.32 | 31.28 | 31.93 | 32.46 | 32.32 | 32.54 | 32.67 | 33.06 | 33.07 | 31.99 | 33.02 |
| O2-O9 | 61.5 | 40.79 | 41.52 | 40.91 | 41.39 | 41.47 | 40.91 | 41.13 | 42.01 | 42.00 | 42.25 | 42.33 | 42.69 | 43.26 | 43.33 |
| O2-O8 | 53.2 | 63.81 | 63.67 | 63.64 | 63.10 | 63.33 | 63.25 | 63.29 | 62.81 | 62.97 | 62.61 | 62.80 | 62.40 | 62.70 | 62.62 |
| O2-O5 | 61.5 | 62.25 | 62.23 | 62.55 | 62.98 | 63.87 | 64.15 | 64.18 | 63.98 | 64.33 | 64.58 | 64.75 | 64.47 | 65.26 | 64.65 |
| O3-O5 | 29.9 | 13.68 | 13.98 | 13.05 | 13.10 | 12.47 | 12.02 | 11.46 | 11.93 | 11.56 | 11.64 | 11.57 | 12.06 | 11.18 | 11.71 |
| O2-O3 | 74.3 | 86.69 | 87.41 | 87.47 | 87.83 | 88.45 | 88.63 | 88.64 | 89.19 | 89.63 | 89.89 | 89.75 | 89.33 | 89.71 | 89.14 |
| O5-O6 | 74.3 | 80.45 | 80.35 | 80.54 | 80.37 | 80.85 | 81.14 | 81.17 | 81.17 | 81.44 | 81.28 | 81.53 | 81.25 | 81.25 | 81.69 |
| O3 -O6 | 53.2 | 57.05 | 57.54 | 57.88 | 57.78 | 58.11 | 58.46 | 58.73 | 59.02 | 59.53 | 59.43 | 59.37 | 59.66 | 59.67 | 59.85 |
| O10-O3 | 74.3 | 72.70 | 72.39 | 72.08 | 71.85 | 71.41 | 71.10 | 70.54 | 70.02 | 69.50 | 69.50 | 69.21 | 68.65 | 68.80 | 67.86 |
| O9-O8 | 61.5 | 68.95 | 68.61 | 68.48 | 67.87 | 67.32 | 67.16 | 67.06 | 66.82 | 66.48 | 66.52 | 66.14 | 66.11 | 65.35 | 65.52 |
| O8-O5 | 61.5 | 57.52 | 57.45 | 57.87 | 57.78 | 57.83 | 57.87 | 57.83 | 58.56 | 58.19 | 58.03 | 57.95 | 58.62 | 57.91 | 58.68 |
| $SM_{tdh}$ | 0 | 11.01 | 10.77 | 10.81 | 10.70 | 10.66 | 10.70 | 10.77 | 10.56 | 10.58 | 10.57 | 10.64 | 10.44 | 10.41 | 10.34 |
| $SM_{Gd}$ | - | 2.01 | 1.78 | 1.44 | 1.24 | 0.89 | 0.70 | 0 | 0.65 | 0.69 | 0.72 | 0.74 | 0.94 | 1.27 | 1.26 |

## 1.5 Trends in Bond Lengths and O-O Distances vs. f Electron Configuration

Bond lengths:

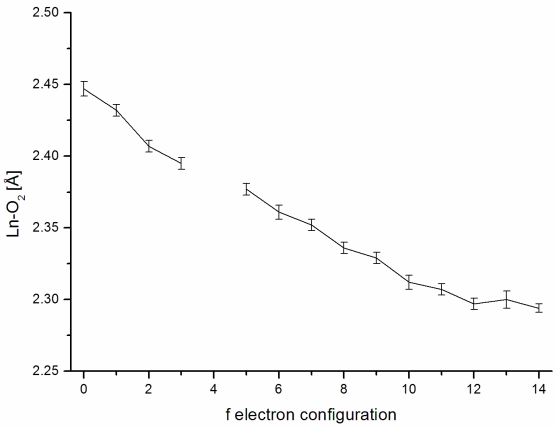



Figure S1. Bond length Ln-O2 vs. f electronic configuration.

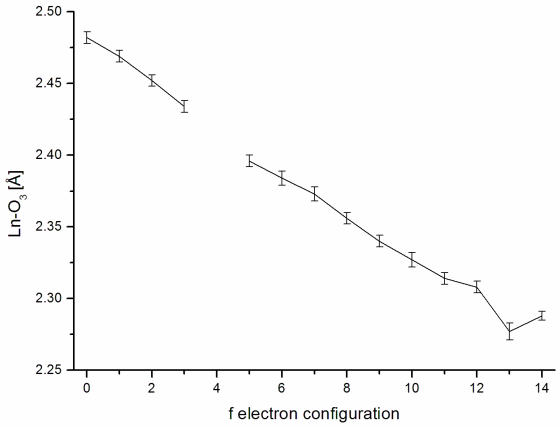



Figure S2. Bond length Ln-O3 vs. f electronic configuration.

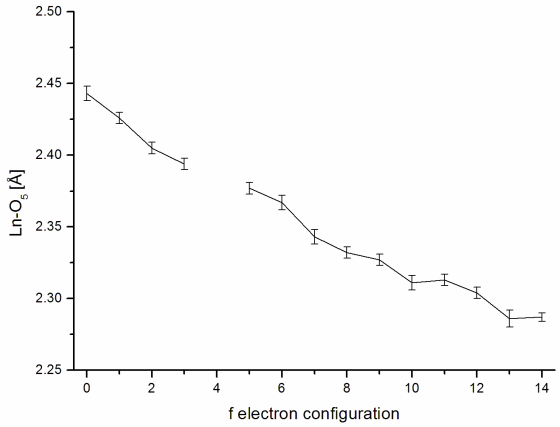



Figure S3. Bond length Ln-O5 vs. f electronic configuration.

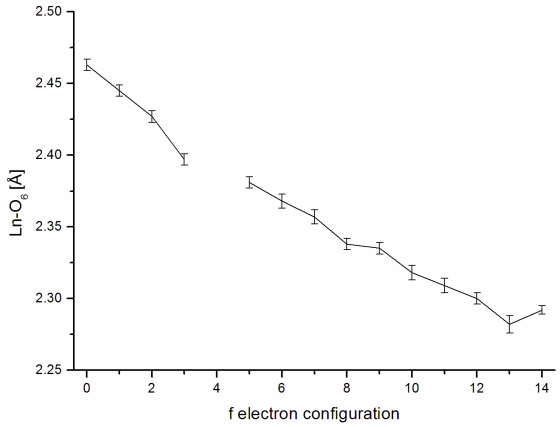



Figure S4. Bond length Ln-O6 vs. f electronic configuration.

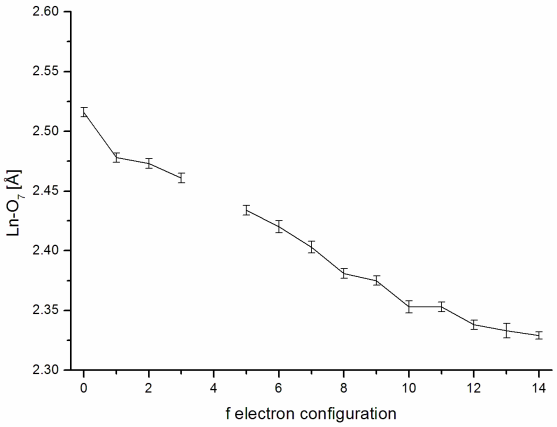



Figure S5. Bond length Ln-O7 vs. f electronic configuration.

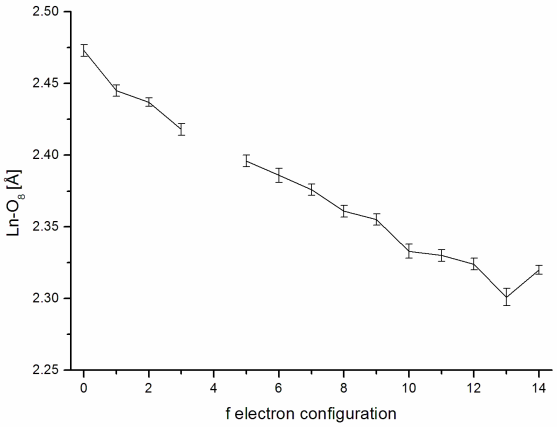



Figure S6. Bond length Ln-O8 vs. f electronic configuration.

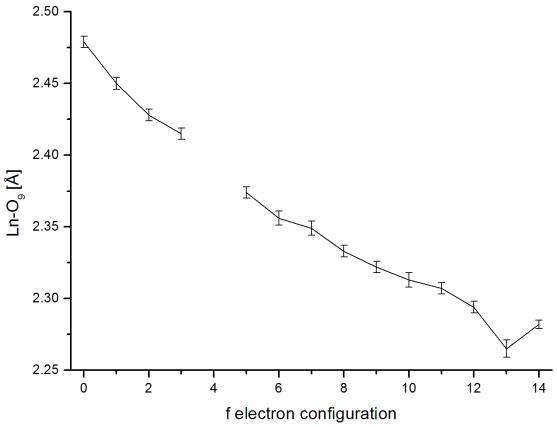



Figure S7. Bond length Ln-O9 vs. f electronic configuration.

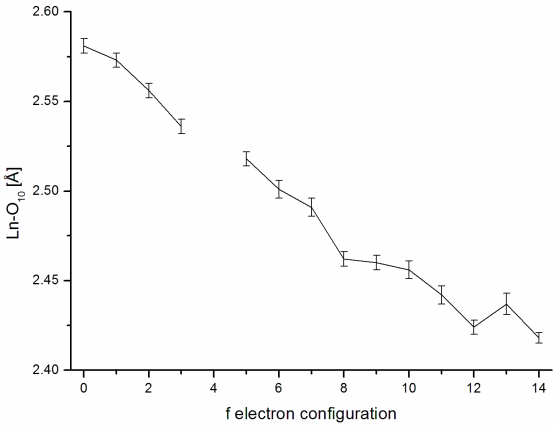



Figure S8. Bond length Ln-O10 vs. f electronic configuration.

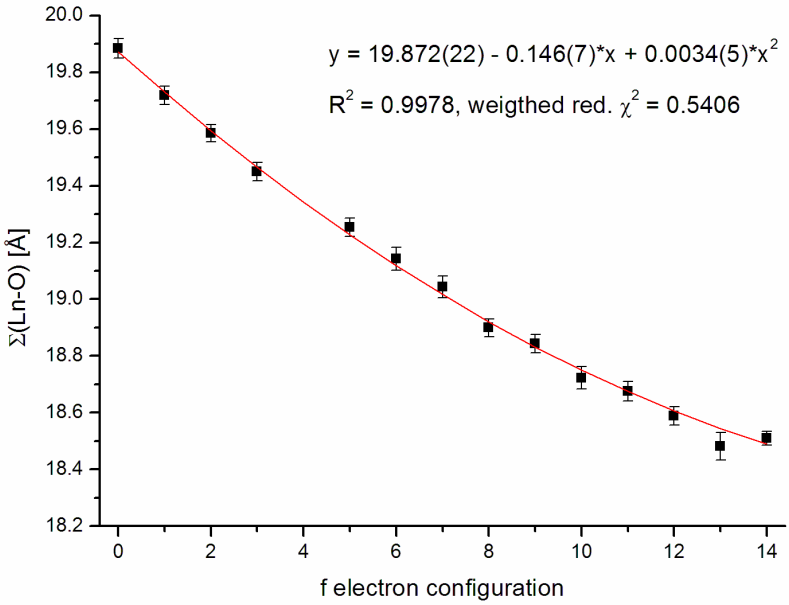



Figure S9. Sum of bond lengths Ln-O vs. f electronic configuration. Quadratic fit ($\chi^2$-weighting factor: $su^{-2}$).

Distances O-O:

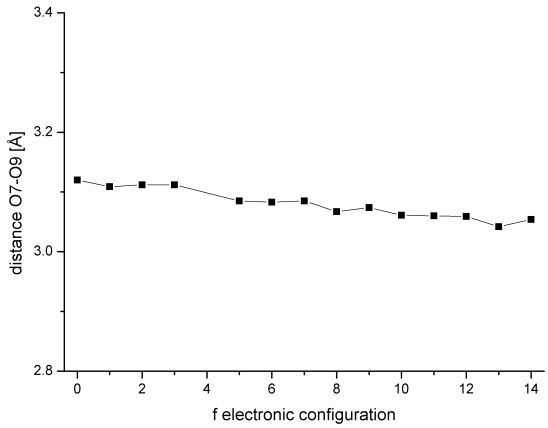



Figure S10. Distance O7-O9 vs. f electronic configuration.

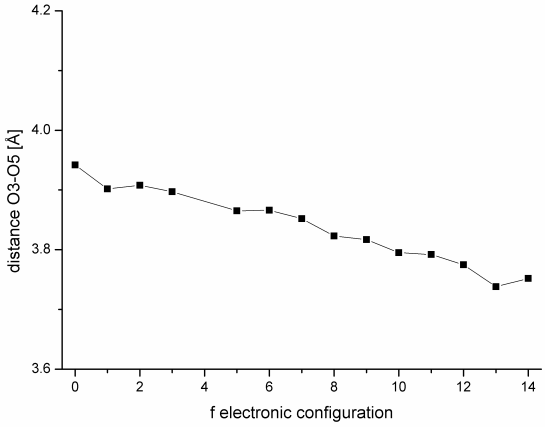



Figure S11. Distance O3-O5 vs. f electronic configuration.

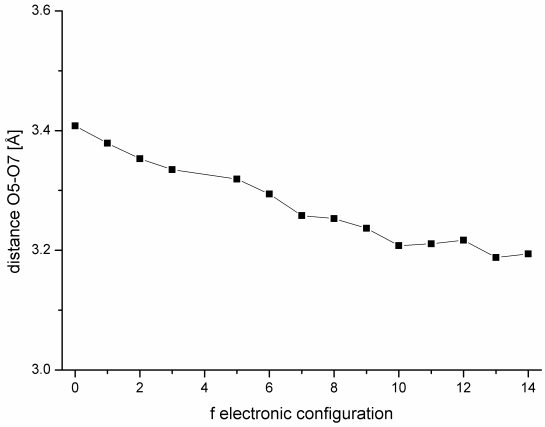



Figure S12. Distance O7-O5 vs. f electronic configuration.

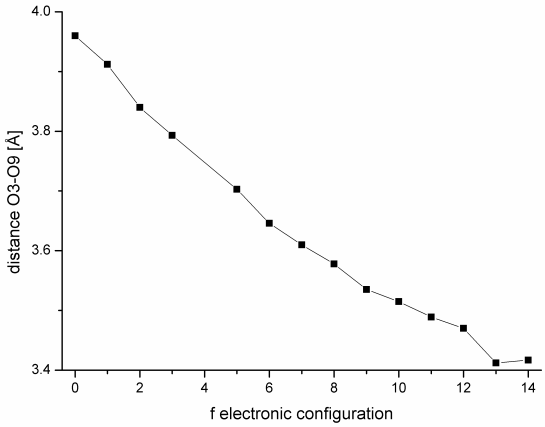



Figure S13. Distance O3-O9 vs. f electronic configuration.

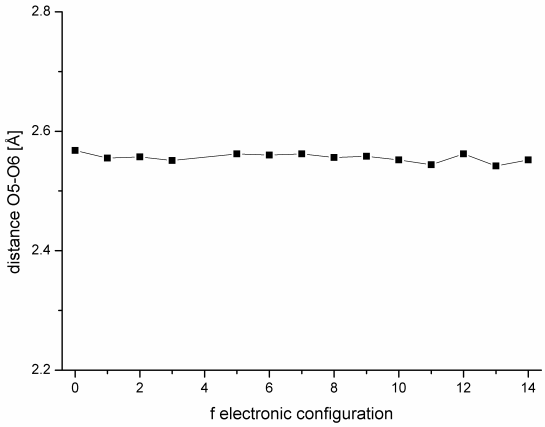



Figure S14. Distance O5-O6 vs. f electronic configuration.

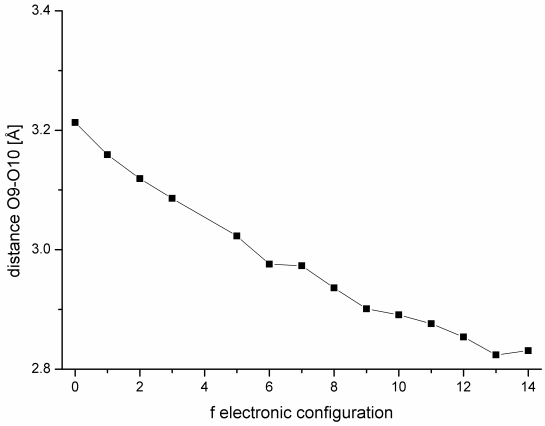



Figure S15. Distance O9-O10 vs. f electronic configuration.

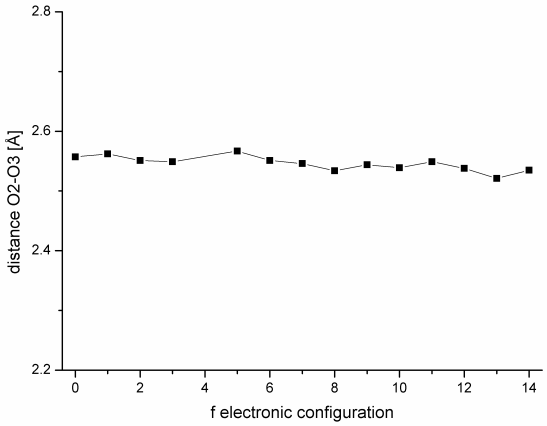



Figure S16. Distance O2-O3 vs. f electronic configuration.

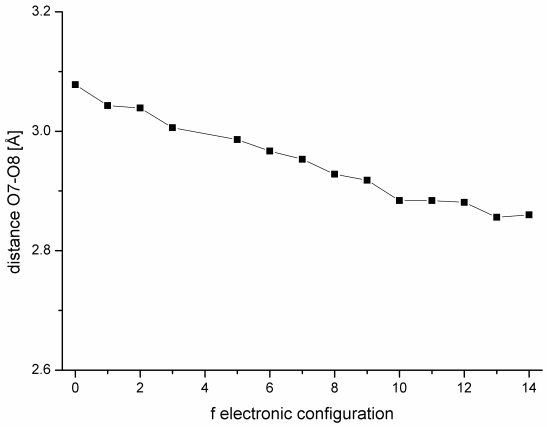



Figure S17. Distance O7-O8 vs. f electronic configuration.

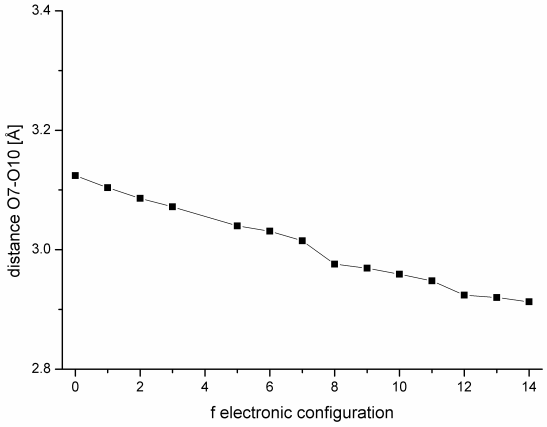



Figure S18. Distance O7-O10 vs. f electronic configuration.

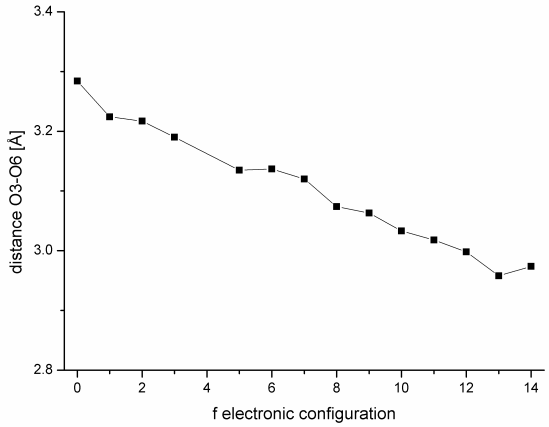



Figure S19. Distance O3-O6 vs. f electronic configuration.

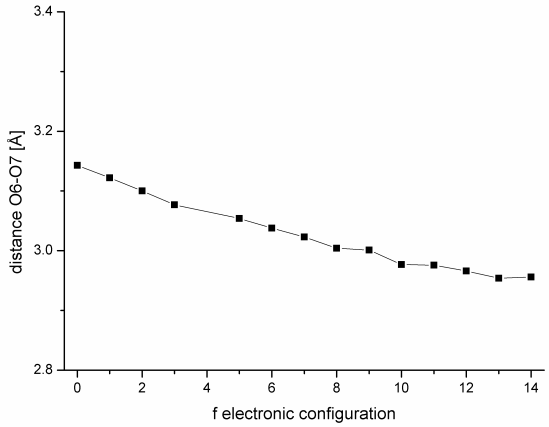



Figure S20. Distance O7-O6 vs. f electronic configuration.

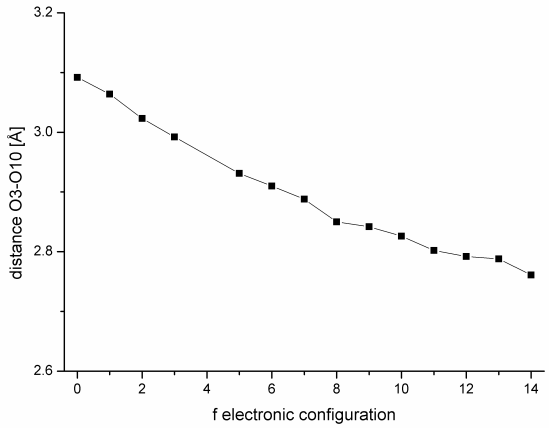



Figure S21. Distance O10-O3 vs. f electronic configuration.

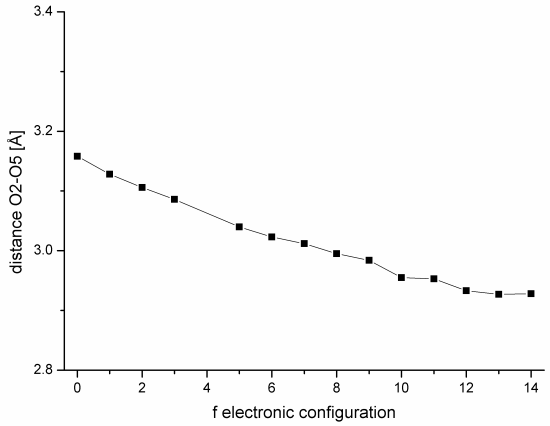



Figure S22. Distance O2-O5 vs. f electronic configuration.

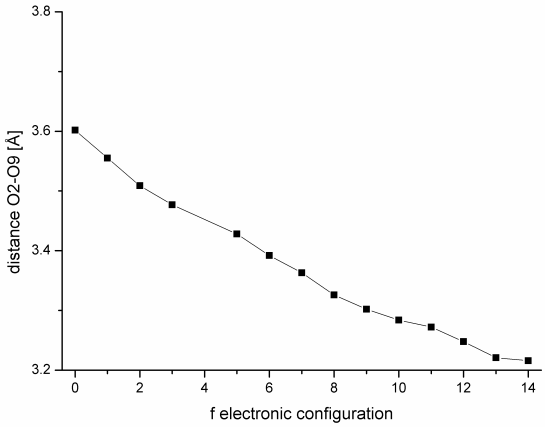



Figure S23. Distance O2-O9 vs. f electronic configuration.

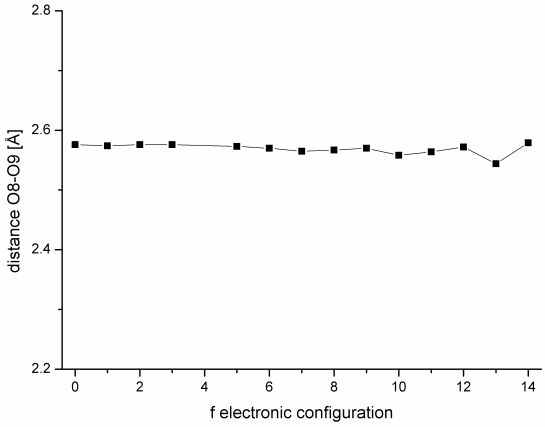



Figure S24. Distance O8-O9 vs. f electronic configuration.

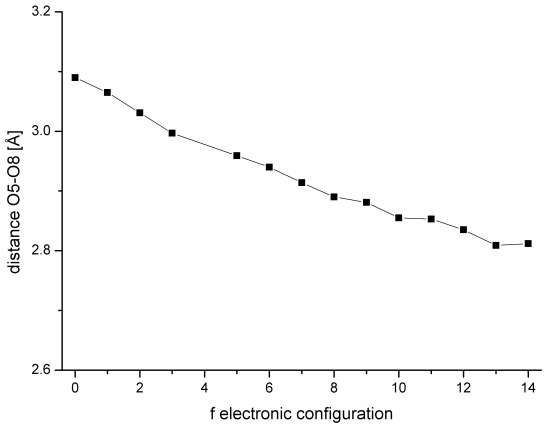



Figure S25. Distance O8-O5 vs. f electronic configuration.

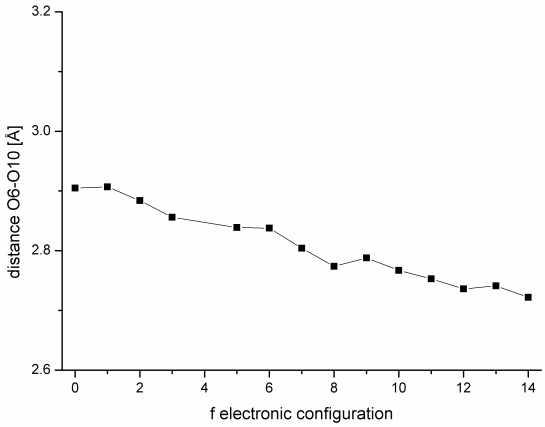



Figure S26. Distance O6-O10 vs. f electronic configuration.

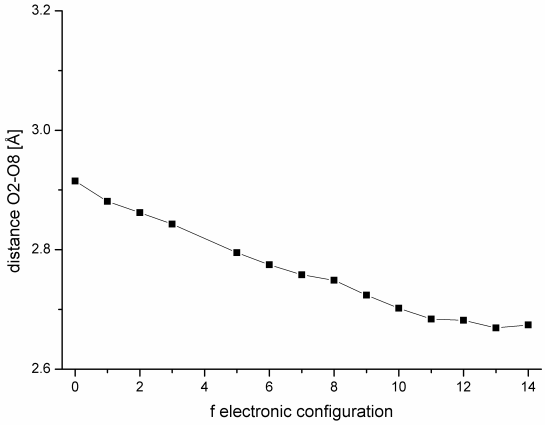



Figure S27. Distance O2-O8 vs. f electronic configuration.

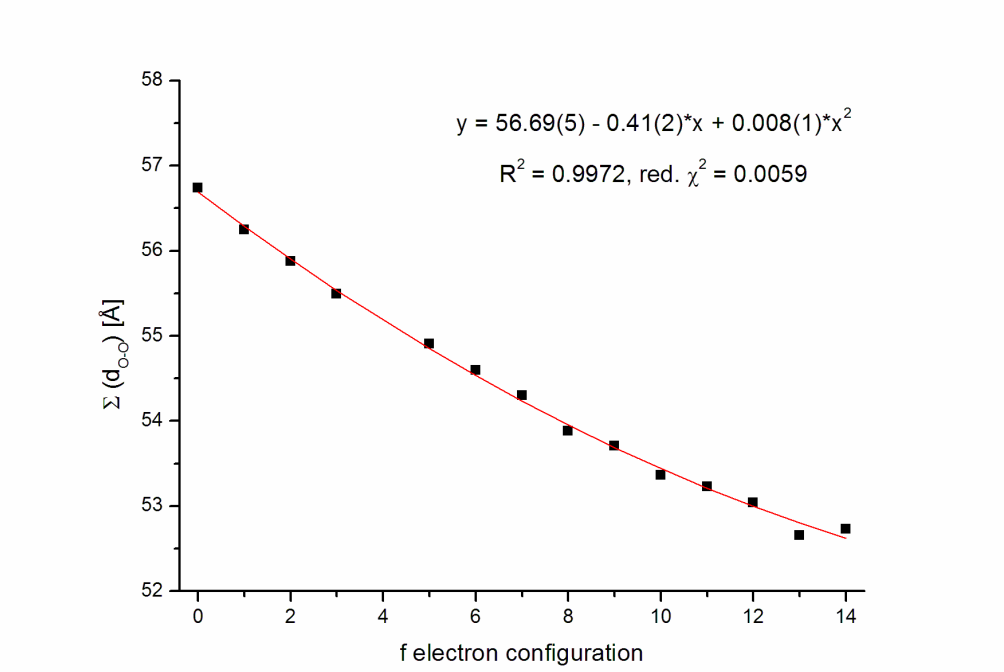
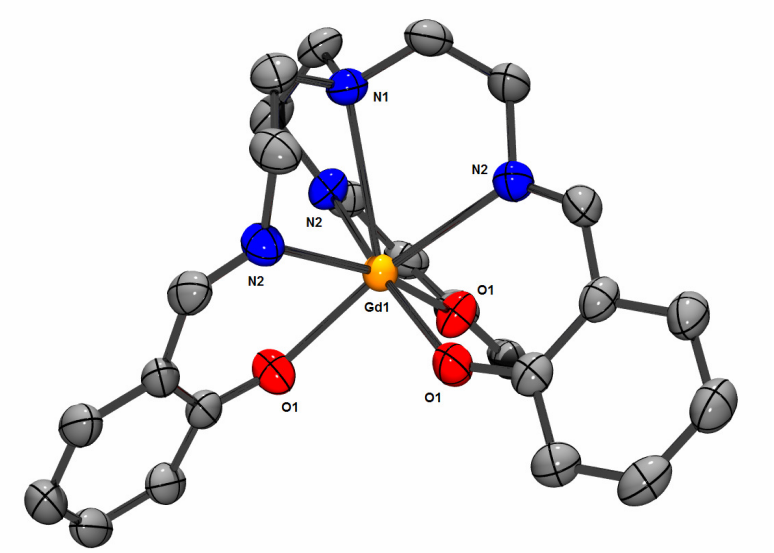



Figure S28. Sum of distance O-O vs. f electronic configuration. Quadratic fit.

## 2. TREN-SAL Lanthanide Complexes[4-7]

### 2.1 Structure




Asymmetric unit of [Gd(TREN-SAL)].[4] Thermal ellipsoid plot (Ortep 3 for Windows,[1] 50% probability level) with atom numbering scheme. Hydrogens omitted for clarity.

### 2.2 Bond Lengths

Table S4. Bond lengths in TREN-SAL lanthanide complexes.[4-7]

| f electrons (Ln) | $d_{Ln-N1}$ (su) [Å] (1x) | $d_{Ln-N2}$ (su) [Å] (3x) | $d_{Ln-O1}$ (su) [Å] (3x) | $\Sigma d_{Ln-X}$ (su) [Å] |
|---|---|---|---|---|
| 0 (La) | - | - | - | - |
| 1 (Ce)[4] | 2.834(4) | 2.605(3) | 2.288(3) | 17.513(22) |
| 2 (Pr)[4] | 2.814(6) | 2.577(5) | 2.282(5) | 17.391(36) |
| 3 (Nd)[4] | 2.796(5) | 2.573(4) | 2.273(3) | 17.334(26) |
| 4 (Pm) | - | - | - | - |
| 5 (Sm)[5] | 2.773(4) | 2.531(3) | 2.247(3) | 17.107(22) |
| 6 (Eu)[5] | 2.761(9) | 2.535(7) | 2.233(6) | 17.065(48) |
| 7 (Gd)[4] | 2.746(4) | 2.511(3) | 2.232(2) | 16.975(19) |
| 8 (Tb)[5] | 2.732(7) | 2.489(5) | 2.214(4) | 16.841(34) |
| 9 (Dy)[6] | 2.738(6) | 2.480(4) | 2.201(4) | 16.781(30) |
| 10 (Ho)[6] | 2.703(9) | 2.472(5) | 2.193(6) | 16.698(42) |
| 11 (Er)[7] | 2.716(8) | 2.455(6) | 2.188(5) | 16.645(41) |
| 12 (Tm)[7] | 2.713(8) | 2.449(6) | 2.167(5) | 16.561(41) |
| 13 (Yb)[4] | 2.694(10) | 2.430(7) | 2.160(6) | 16.464(49) |
| 14 (Lu)[7] | 2.722(8) | 2.426(6) | 2.162(5) | 16.486(41) |
| $d_{Ce}$ / $d_{Lu}$ | 1.041 | 1.074 | 1.058 | 1.062 |

## 2.3 X-X Distances

Table S5. X-X Distances in TREN-SAL lanthanide complexes.[4-7]

| f electrons (Ln) | $d_{N1-N2}$ [Å] (3x) | $d_{N2-N2'}$ [Å] (3x) | $d_{N2-O1}$ [Å] (3x) | $d_{N2-O1'}$ [Å] (3x) | $d_{O1-O1'}$ [Å] (3x) | $\Sigma d_{X-X}$ [Å] |
|---|---|---|---|---|---|---|
| 0 (La) | - | - | - | - | - | - |
| 1 (Ce)[4] | 2.909 | 4.073 | 2.833 | 3.424 | 3.481 | 50.160 |
| 2 (Pr)[4] | 2.900 | 4.042 | 2.821 | 3.394 | 3.454 | 49.833 |
| 3 (Nd)[4] | 2.908 | 4.055 | 2.819 | 3.374 | 3.425 | 49.743 |
| 4 (Pm) | - | - | - | - | - | |
| 5 (Sm)[5] | 2.881 | 3.994 | 2.826 | 3.295 | 3.364 | 49.080 |
| 6 (Eu)[5] | 2.874 | 3.997 | 2.843 | 3.272 | 3.335 | 48.963 |
| 7 (Gd)[4] | 2.871 | 3.973 | 2.826 | 3.273 | 3.305 | 48.744 |
| 8 (Tb)[5] | 2.856 | 3.943 | 2.813 | 3.219 | 3.285 | 48.348 |
| 9 (Dy)[6] | 2.858 | 3.931 | 2.813 | 3.202 | 3.254 | 48.174 |
| 10 (Ho)[6] | 2.840 | 3.923 | 2.819 | 3.187 | 3.223 | 47.976 |
| 11 (Er)* | - | - | - | - | - | |
| 12 (Tm)* | - | - | - | - | - | |
| 13 (Yb)[4] | 2.836 | 3.873 | 2.794 | 3.102 | 3.163 | 47.304 |
| 14 (Lu)* | - | - | - | - | - | - |
| $d_{Ce}$ / $d_{Lu}$ | 1.026 | 1.052 | 1.014 | 1.104 | 1.101 | 1.060 |

* Coordinates were not available for the calculation of X-X distances.

## 2.4 Trends in Bond Lengths and X-X Distances vs. f Electron Configuration

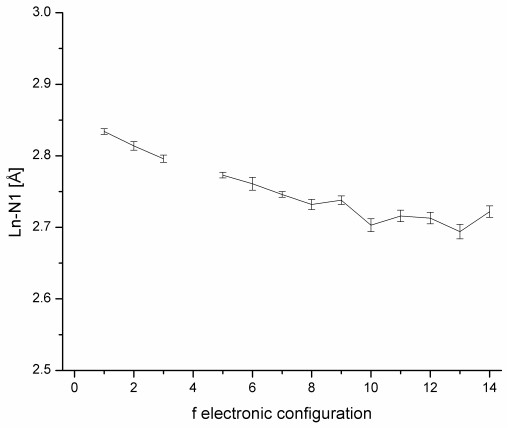



Figure S29. Bond length Ln-N1 vs. f electronic configuration.

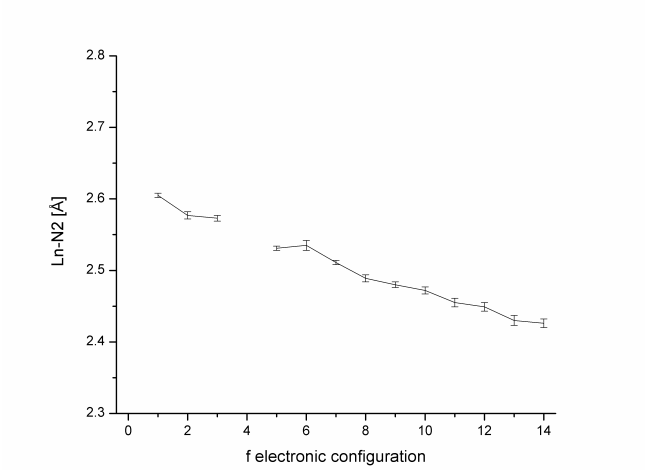



Figure S30. Bond length Ln-N2 vs. f electronic configuration.

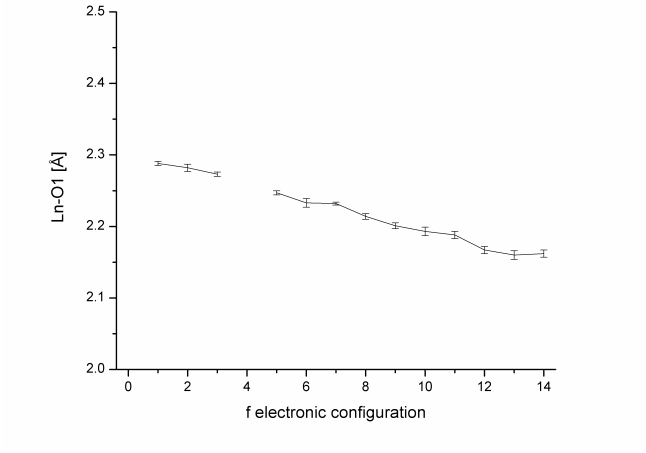



Figure S31. Bond length Ln-O1 vs. f electronic configuration.

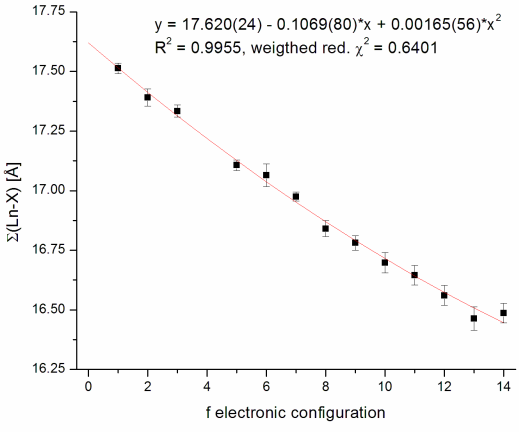



Figure S32. Sum of bond lengths Ln-X (X = N, O) vs. f electronic configuration. Quadratic fit ($\chi^2$- weighting factor: $su^{-2}$).

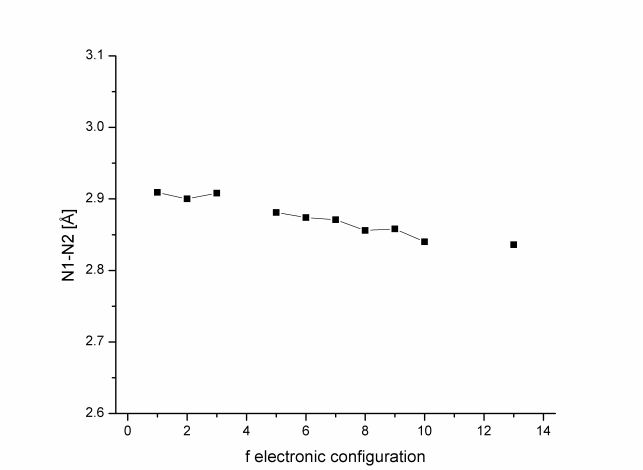



Figure S33. Distance N1-N2 vs. f electronic configuration.

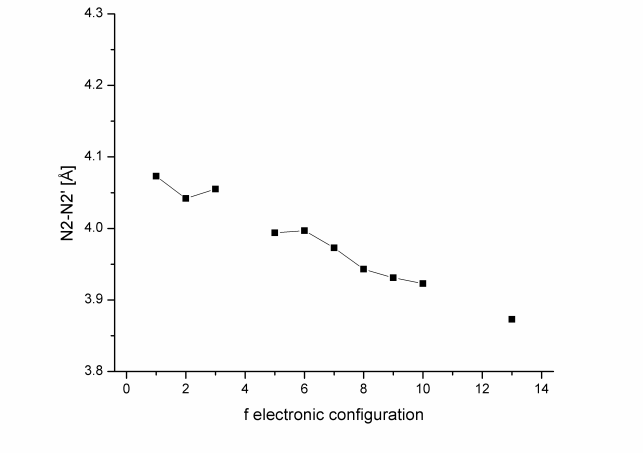



Figure S34. Distance N2-N2’ vs. f electronic configuration.

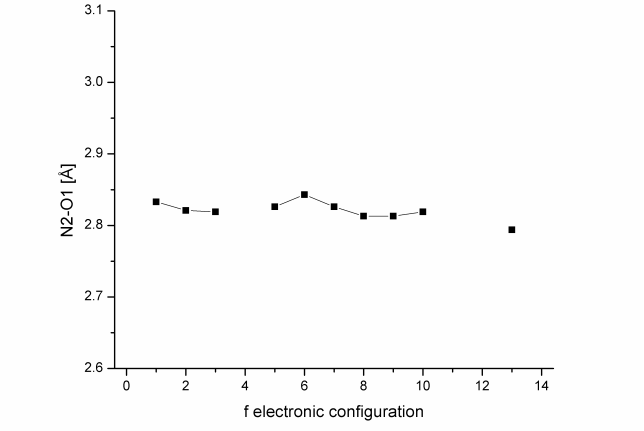



Figure S35. Distance N2-O1 vs. f electronic configuration.

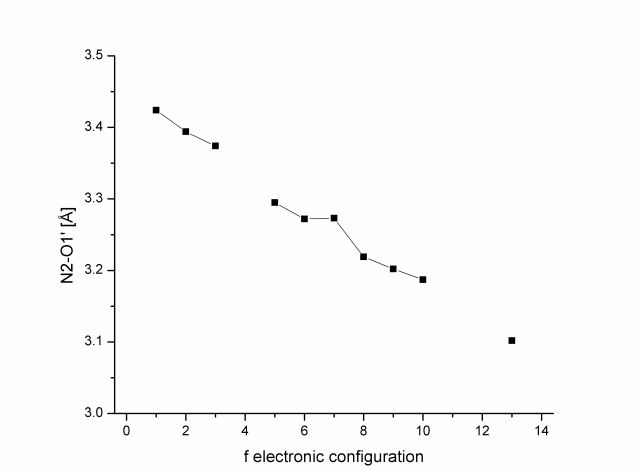



Figure S36. Distance N2-O1’ vs. f electronic configuration.

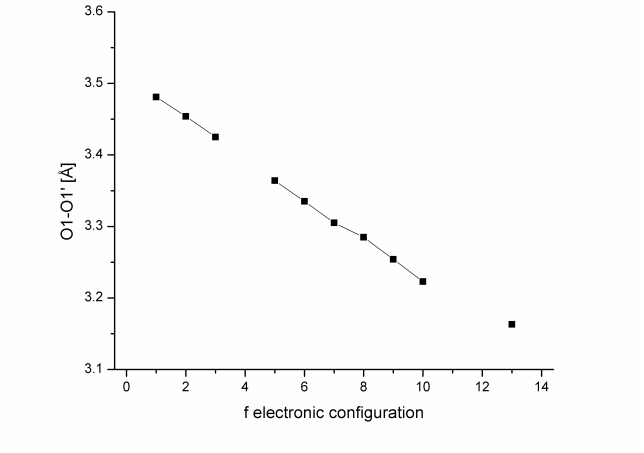



Figure S37. Distance O1-O1’ vs. f electronic configuration.

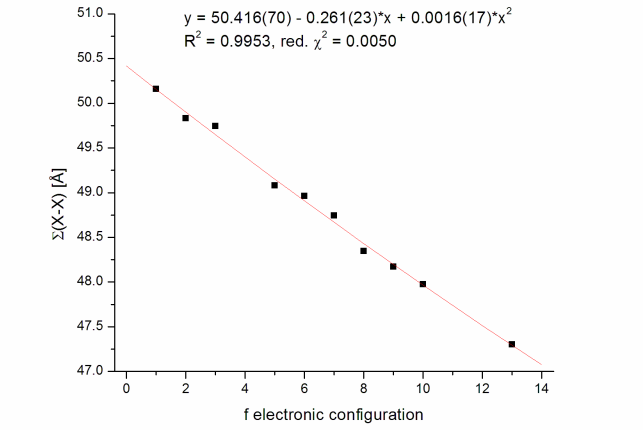
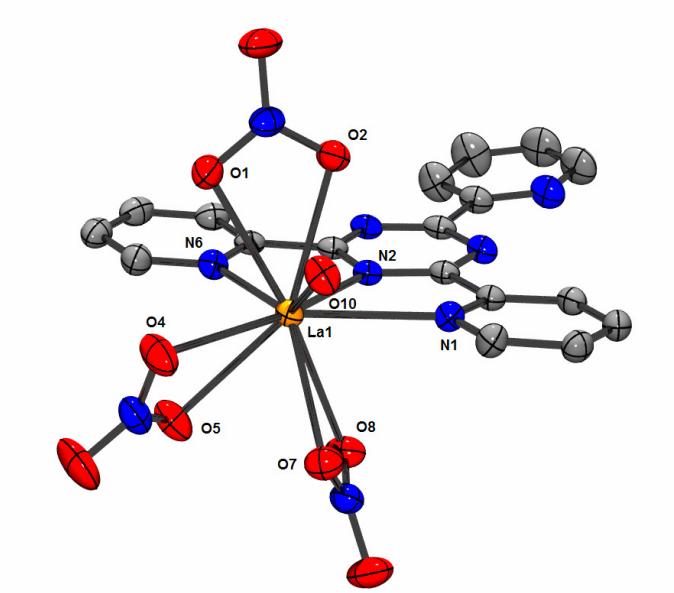



Figure S38. Sum of Distances X-X (X = N, O; bound to Ln) vs. f electronic configuration. Quadratic fit.

## 3. [Ln(tptz)$(NO_3)_3(H_2O)$] Complexes[8]

### 3.1 Structure




Asymmetric unit of [La(tptz)$(NO_3)_3(H_2O)$]*2EtOH.[8] Thermal ellipsoid plot (Ortep 3 for Windows,[1] 50% probability level) with atom numbering scheme. Hydrogens and the two isolated ethanol molecules omitted for clarity.

### 3.2 Bond Lengths

Table S6. Bond lengths in [Ln(tptz)$(NO_3)_3(H_2O)$].[8]

| f electrons (Ln) | $d_{Ln-N1}$ (su) [Å] | $d_{Ln-N2}$ (su) [Å] | $d_{Ln-N6}$ (su) [Å] | $d_{Ln-O1}$ (su) [Å] | $d_{Ln-O2}$ (su) [Å] | $d_{Ln-O4}$ (su) [Å] | $d_{Ln-O5}$ (su) [Å] | $d_{Ln-O7}$ (su) [Å] | $d_{Ln-O8}$ (su) [Å] | $d_{Ln-O10}$ (su) [Å] | $\Sigma d_{Ln-X}$ (su) [Å] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | 2.667(2) | 2.691(1) | 2.703(1) | 2.617(1) | 2.570(1) | 2.588(2) | 2.631(1) | 2.595(1) | 2.631(1) | 2.452(1) | 26.145(12) |
| 1 (Ce) | 2.660(4) | 2.678(4) | 2.696(4) | 2.598(4) | 2.549(4) | 2.565(4) | 2.618(4) | 2.585(4) | 2.611(4) | 2.424(4) | 25.984(40) |
| 2 (Pr) | 2.630(3) | 2.644(3) | 2.668(3) | 2.583(3) | 2.524(3) | 2.546(3) | 2.594(3) | 2.556(2) | 2.592(3) | 2.412(3) | 25.749(29) |
| 3 (Nd) | 2.614(3) | 2.629(3) | 2.658(3) | 2.568(3) | 2.506(3) | 2.534(3) | 2.584(3) | 2.541(3) | 2.584(3) | 2.400(3) | 25.618(30) |
| 4 (Pm) | - | - | - | - | - | - | - | - | - | - | - |
| 5 (Sm) | 2.593(2) | 2.603(2) | 2.629(2) | 2.546(2) | 2.481(2) | 2.505(2) | 2.566(2) | 2.511(2) | 2.557(2) | 2.368(2) | 25.359(20) |
| 6 (Eu) | 2.576(2) | 2.579(2) | 2.619(2) | 2.536(2) | 2.465(2) | 2.490(2) | 2.558(2) | 2.496(2) | 2.544(2) | 2.349(2) | 25.212(20) |
| 7 (Gd) | 2.569(2)* | 2.567(2)* | 2.607(2) | 2.532(2) | 2.456(2) | 2.485(2)* | 2.555(2) | 2.481(2)* | 2.538(2) | 2.337(2) | 25.127(20) |
| 8 (Tb) | 2.555(2)* | 2.545(2)* | 2.592(2) | 2.523(2)* | 2.439(2) | 2.464(2) | 2.552(2) | 2.467(2) | 2.520(2)* | 2.322(2) | 24.979(20) |
| 9 (Dy) | 2.547(2)* | 2.534(2)* | 2.582(2) | 2.516(2)* | 2.426(2) | 2.451(2) | 2.545(2) | 2.453(2) | 2.515(2)* | 2.311(2) | 24.880(20) |
| 10 (Ho) | 2.537(2)* | 2.524(2)* | 2.573(2) | 2.512(2)* | 2.416(1) | 2.442(2) | 2.544(2) | 2.442(1) | 2.506(2)* | 2.303(2) | 24.799(18) |
| 11 (Er) | 2.528(2)* | 2.513(2)* | 2.562(3) | 2.503(3)* | 2.401(3) | 2.429(2) | 2.544(3) | 2.432(2) | 2.495(2)* | 2.292(3) | 24.699(25) |
| 12 (Tm) | 2.508(4) | 2.508(4) | 2.519(3) | 2.542(3)* | 2.404(3) | 2.419(3) | 2.520(3)* | 2.437(3) | 2.528(3) | 2.262(3) | 24.647(32) |
| 13 (Yb) | 2.510(2)* | 2.490(2)* | 2.541(2) | 2.504(2)* | 2.377(2) | 2.399(2) | 2.567(2) | 2.413(2) | 2.482(2)* | 2.270(2) | 24.553(20) |
| 14 (Lu) | - | - | - | - | - | - | - | - | - | - | - |
| $d_{La}$ / $d_{Yb}$ | 1.063 | 1.081 | 1.064 | 1.080 | 1.081 | 1.079 | 1.075 | 1.045 | 1.060 | 1.025 | 1.065 |

* Bond lengths taken from the published cif-files. Incorrectly listed in the original publication (see ref. 8).

## 3.3 X-X Distances

Table S7. Distances X-X (X = N,O bound to Ln) in $[Ln(tptz)(NO_3)_3(H_2O)]$.[8]

| f electrons (Ln) | $d_{N1-N2}$ [Å] | $d_{N1-O2}$ [Å] | $d_{N1-O10}$ [Å] | $d_{N1-O7}$ [Å] | $d_{N1-O8}$ [Å] | $d_{N2-O2}$ [Å] | $d_{O2-O10}$ [Å] | $d_{O10-O7}$ [Å] | $d_{O7-O8}$ [Å] | $d_{O8-N2}$ [Å] | $d_{N6-O1}$ [Å] | $d_{O1-O4}$ [Å] | $d_{O4-O5}$ [Å] | $d_{O5-N6}$ [Å] | $d_{N2-N6}$ [Å] | $d_{O1-O2}$ [Å] | $d_{O1-O10}$ [Å] | $d_{O10-O4}$ [Å] | $d_{O4-O7}$ [Å] | $d_{O7-O5}$ [Å] | $d_{O5-O8}$ [Å] | $\Sigma d_{X-X}$ [Å] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | 2.705 | 3.175 | 3.195 | 3.246 | 2.979 | 2.918 | 3.025 | 3.115 | 2.164 | 3.145 | 3.048 | 3.042 | 2.152 | 3.089 | 2.698 | 2.159 | 3.080 | 3.042 | 3.154 | 3.028 | 2.993 | 61.152 |
| 1 (Ce) | 2.715 | 3.157 | 3.176 | 3.237 | 2.967 | 2.900 | 3.002 | 3.084 | 2.165 | 3.124 | 3.045 | 3.014 | 2.161 | 3.078 | 2.700 | 2.162 | 3.039 | 2.974 | 3.100 | 2.981 | 2.949 | 60.730 |
| 2 (Pr) | 2.701 | 3.141 | 3.148 | 3.179 | 2.934 | 2.871 | 2.975 | 3.060 | 2.163 | 3.080 | 3.004 | 2.974 | 2.159 | 3.041 | 2.691 | 2.161 | 3.014 | 2.959 | 3.080 | 2.950 | 2.906 | 60.191 |
| 3 (Nd) | 2.702 | 3.121 | 3.128 | 3.149 | 2.918 | 2.848 | 2.971 | 3.032 | 2.170 | 3.053 | 2.994 | 2.955 | 2.162 | 3.026 | 2.687 | 2.160 | 2.993 | 2.928 | 3.057 | 2.931 | 2.889 | 59.874 |
| 4 (Pm) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 5 (Sm) | 2.703 | 3.099 | 3.087 | 3.111 | 2.902 | 2.833 | 2.928 | 3.004 | 2.168 | 3.001 | 2.945 | 2.906 | 2.155 | 2.990 | 2.677 | 2.163 | 2.958 | 2.890 | 3.017 | 2.887 | 2.842 | 59.266 |
| 6 (Eu) | 2.691 | 3.089 | 3.066 | 3.083 | 2.884 | 2.816 | 2.914 | 2.974 | 2.171 | 2.968 | 2.929 | 2.886 | 2.153 | 2.964 | 2.676 | 2.150 | 2.942 | 2.869 | 3.003 | 2.876 | 2.820 | 58.924 |
| 7 (Gd) | 2.692 | 3.077 | 3.056 | 3.068 | 2.874 | 2.808 | 2.895 | 2.963 | 2.163 | 2.955 | 2.914 | 2.869 | 2.157 | 2.953 | 2.667 | 2.159 | 2.925 | 2.862 | 2.993 | 2.859 | 2.806 | 58.715 |
| 8 (Tb) | 2.688 | 3.065 | 3.031 | 3.043 | 2.859 | 2.789 | 2.881 | 2.945 | 2.158 | 2.920 | 2.901 | 2.846 | 2.152 | 2.936 | 2.659 | 2.153 | 2.911 | 2.838 | 2.972 | 2.840 | 2.788 | 58.375 |
| 9 (Dy) | 2.690 | 3.052 | 3.019 | 3.025 | 2.850 | 2.775 | 2.868 | 2.926 | 2.162 | 2.906 | 2.881 | 2.825 | 2.149 | 2.925 | 2.656 | 2.156 | 2.900 | 2.824 | 2.958 | 2.822 | 2.770 | 58.139 |
| 10 (Ho) | 2.686 | 3.036 | 3.004 | 3.009 | 2.842 | 2.763 | 2.859 | 2.911 | 2.159 | 2.889 | 2.871 | 2.816 | 2.151 | 2.909 | 2.659 | 2.156 | 2.890 | 2.818 | 2.947 | 2.813 | 2.754 | 57.942 |
| 11 (Er) | 2.686 | 3.026 | 2.988 | 2.993 | 2.827 | 2.748 | 2.834 | 2.906 | 2.156 | 2.873 | 2.855 | 2.800 | 2.144 | 2.899 | 2.656 | 2.156 | 2.871 | 2.814 | 2.930 | 2.801 | 2.744 | 57.707 |
| 12 (Tm) | 2.647 | 3.056 | 3.015 | 2.980 | 2.797 | 2.767 | 2.836 | 2.913 | 2.167 | 2.860 | 2.853 | 2.803 | 2.159 | 2.899 | 2.631 | 2.151 | 2.851 | 2.748 | 2.938 | 2.753 | 2.731 | 57.555 |
| 13 (Yb) | 2.677 | 3.007 | 2.974 | 2.977 | 2.826 | 2.729 | 2.825 | 2.876 | 2.162 | 2.836 | 2.842 | 2.776 | 2.141 | 2.888 | 2.642 | 2.148 | 2.861 | 2.788 | 2.906 | 2.785 | 2.719 | 57.385 |
| 14 (Lu) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $d_{La}$ / $d_{Yb}$ | 1.010 | 1.056 | 1.074 | 1.080 | 1.054 | 1.069 | 1.071 | 1.083 | 1.001 | 1.109 | 1.072 | 1.096 | 1.005 | 1.070 | 1.021 | 1.005 | 1.077 | 1.091 | 1.085 | 1.087 | 1.101 | 1.066 |

## 3.4 Trends in Bond Lengths and X-X Distances vs. f Electron Configuration

Bond Lengths:

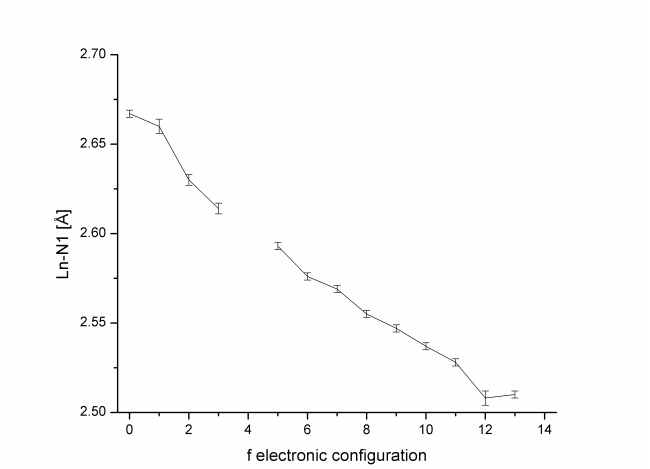



Figure S39. Bond length Ln-N1 vs. f electronic configuration.

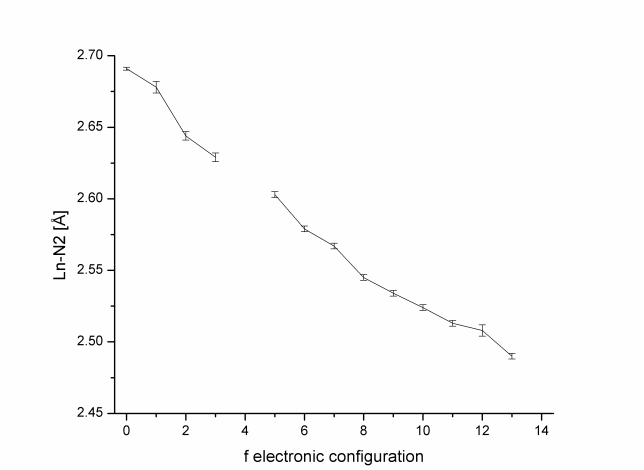



Figure S40. Bond length Ln-N2 vs. f electronic configuration.

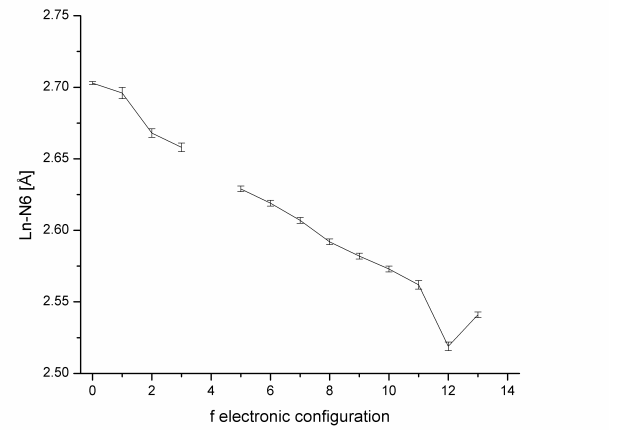



Figure S41. Bond length Ln-N6 vs. f electronic configuration.

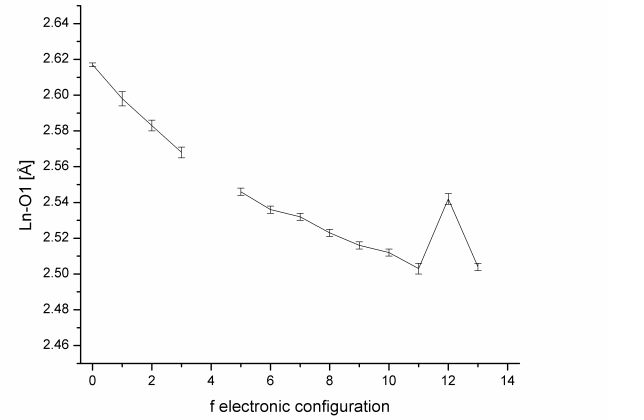



Figure S42. Bond length Ln-O1 vs. f electronic configuration.

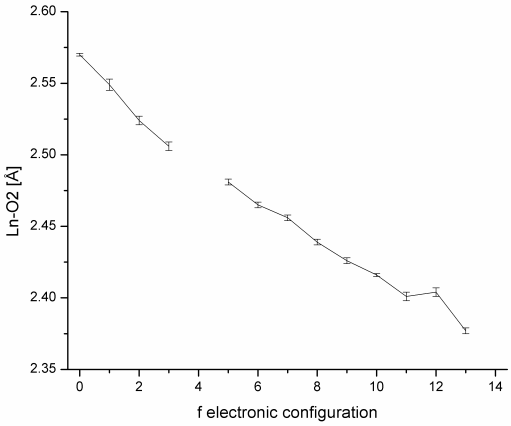



Figure S43. Bond length Ln-O2 vs. f electronic configuration.

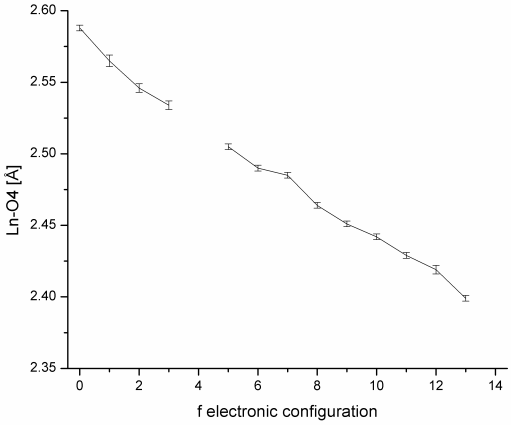



Figure S44. Bond length Ln-O4 vs. f electronic configuration.

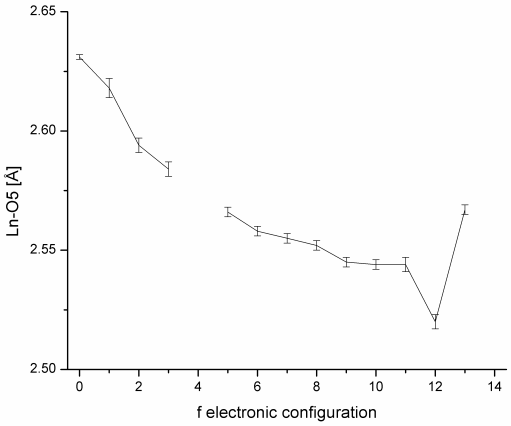



Figure S45. Bond length Ln-O5 vs. f electronic configuration.

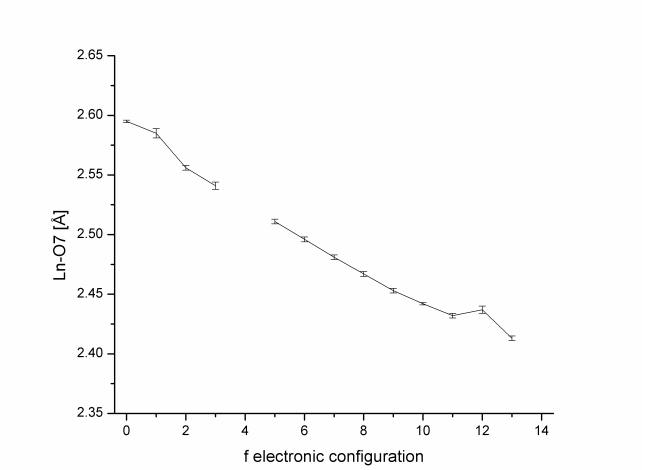



Figure S46. Bond length Ln-O7 vs. f electronic configuration.

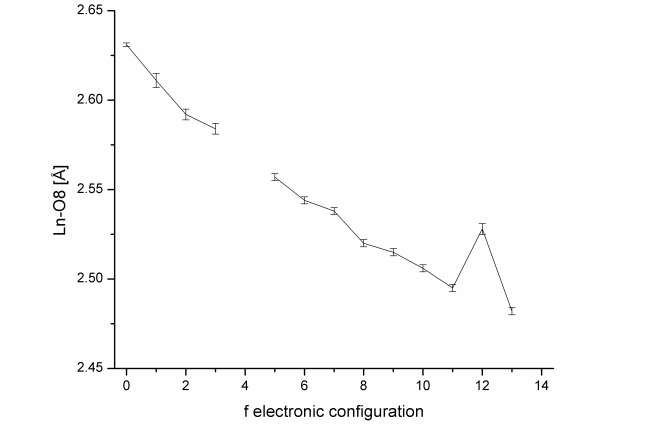



Figure S47. Bond length Ln-O8 vs. f electronic configuration.

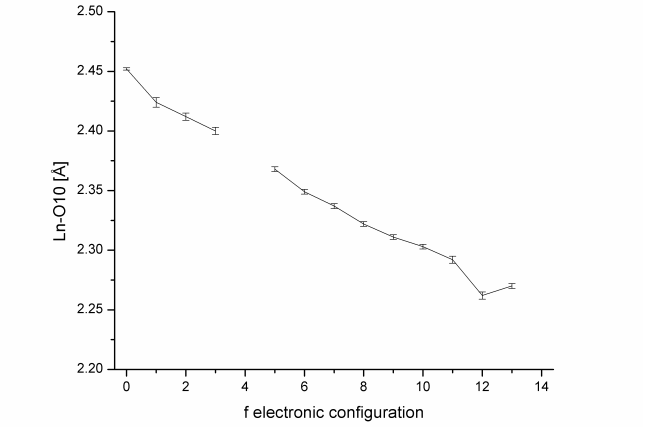



Figure S48. Bond length Ln-O10 vs. f electronic configuration.

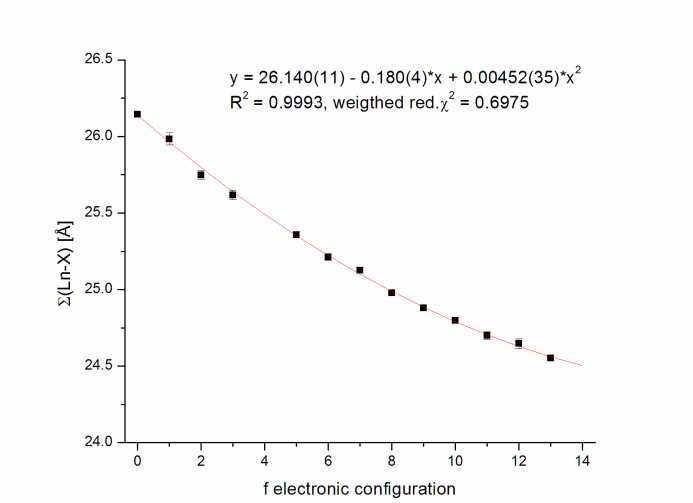



Figure S49. Sum of bond lengths Ln-X Ln-X (X = N, O) vs. f electronic configuration. Quadratic fit ($\chi^2$- weighting factor: $su^{-2}$).

Distances X-X (X = N,O):

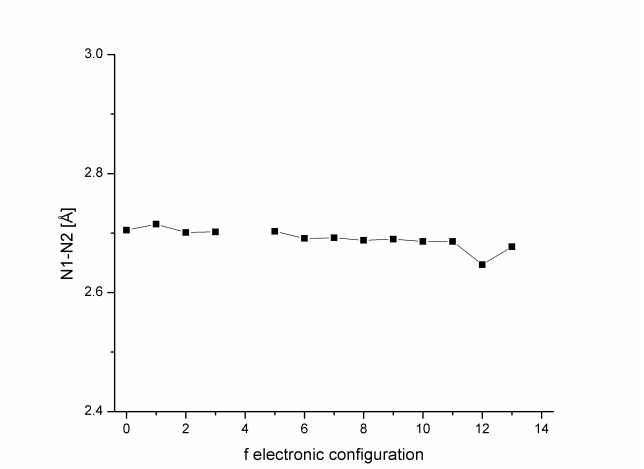



Figure S50. Distance N1-N2 vs. f electronic configuration.

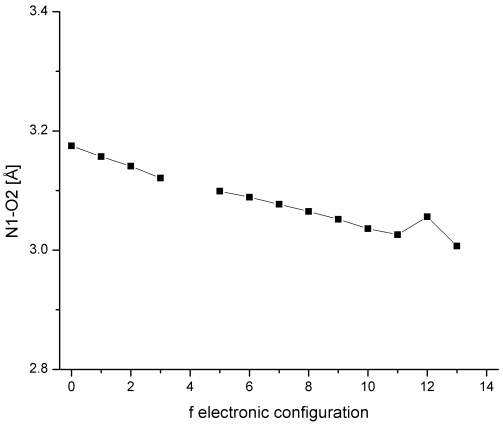



Figure S51. Distance N1-O2 vs. f electronic configuration.

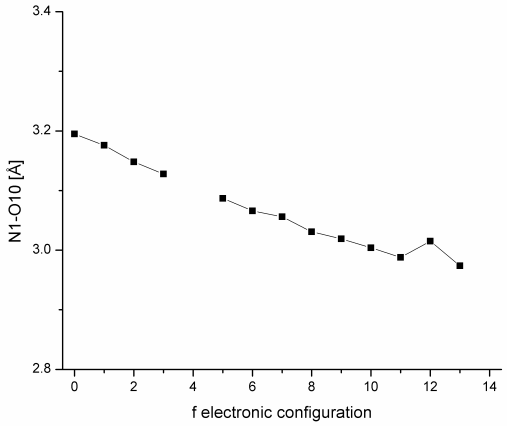



Figure S52. Distance N1-O10 vs. f electronic configuration.

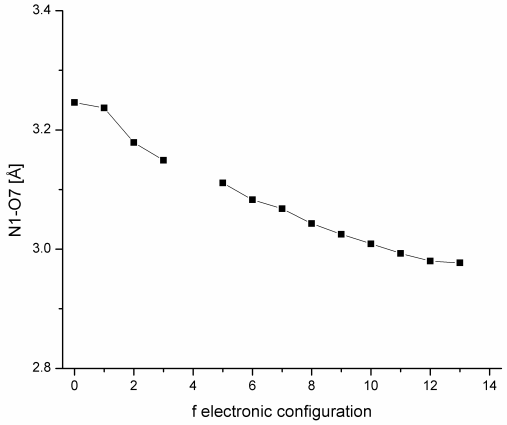



Figure S53. Distance N1-O7 vs. f electronic configuration.

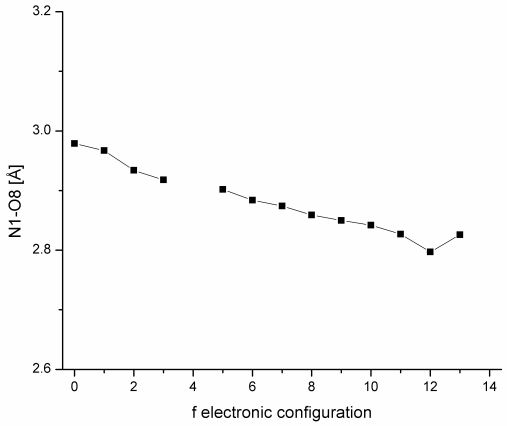



Figure S54. Distance N1-O8 vs. f electronic configuration.

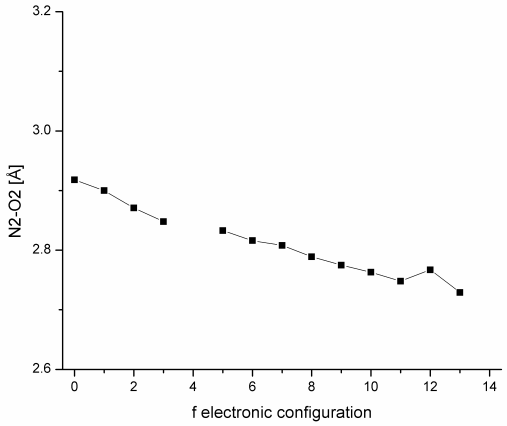



Figure S55. Distance N2-O2 vs. f electronic configuration.

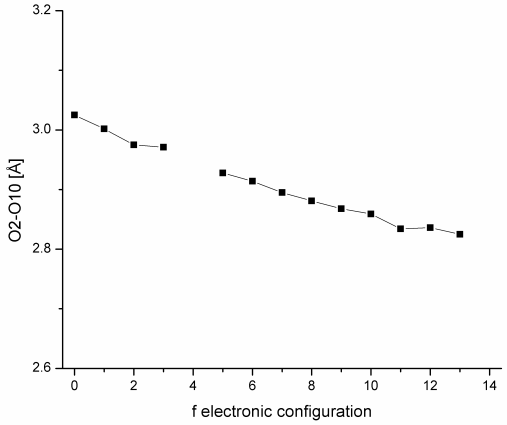



Figure S56. Distance O2-O10 vs. f electronic configuration.

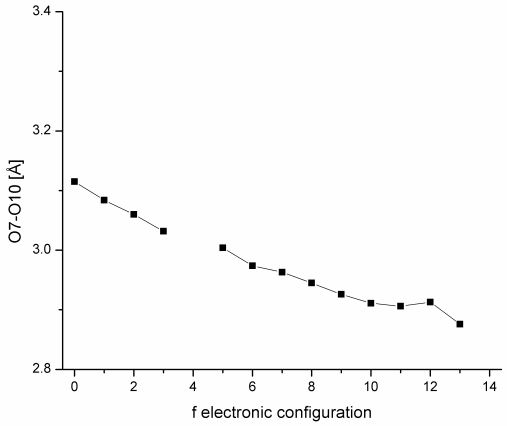



Figure S57. Distance O7-O10 vs. f electronic configuration.

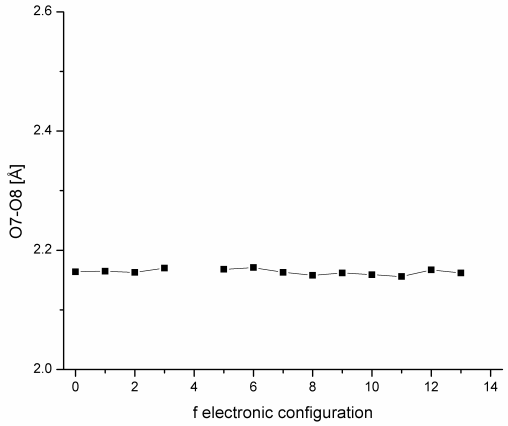



Figure S58. Distance O7-O8 vs. f electronic configuration.

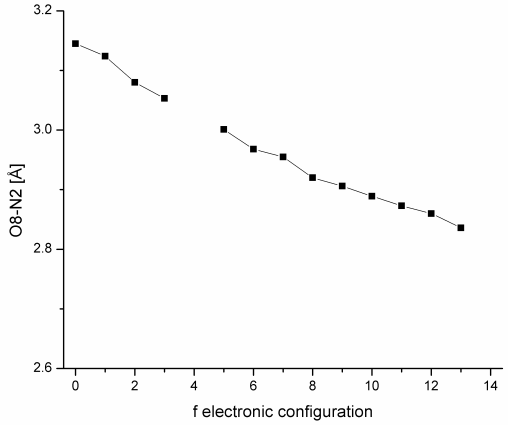



Figure S59. Distance O8-N2 vs. f electronic configuration.

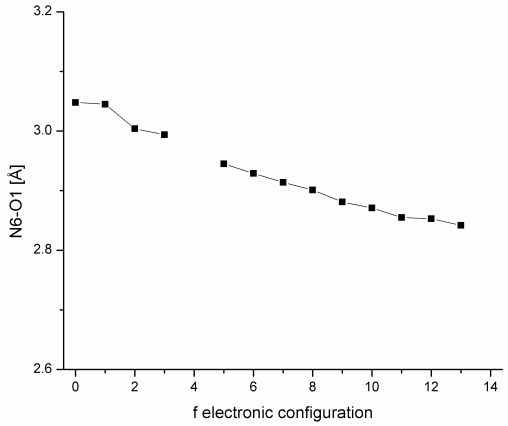



Figure S60. Distance N6-O1 vs. f electronic configuration.

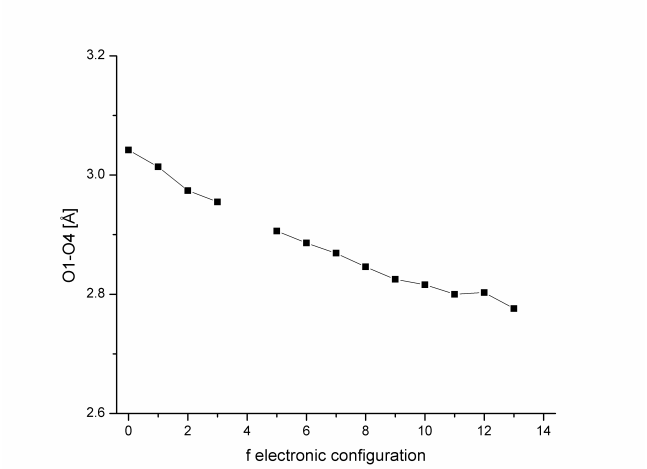



Figure S61. Distance O1-O4 vs. f electronic configuration.

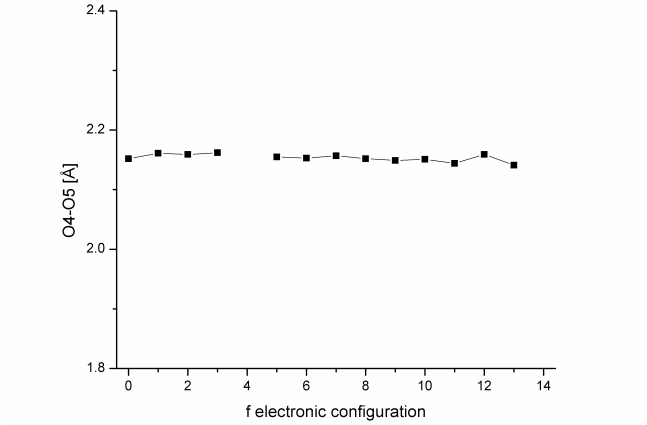



Figure S62. Distance O4-O5 vs. f electronic configuration.

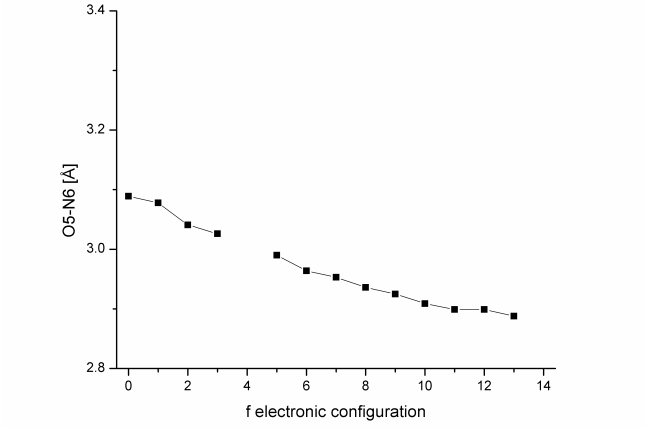



Figure S63. Distance O5-N6 vs. f electronic configuration.

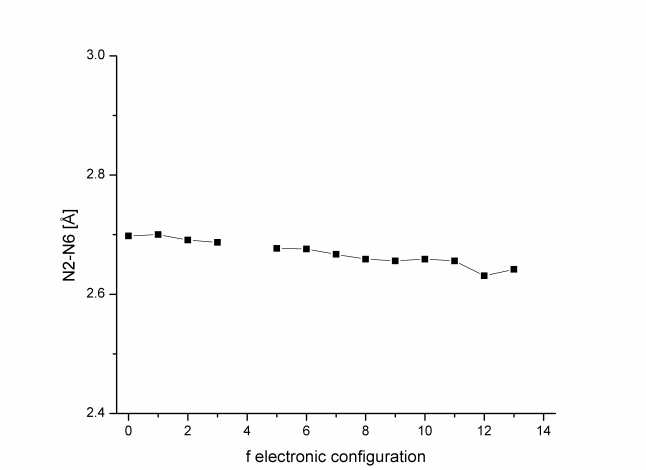



Figure S64. Distance N2-N6 vs. f electronic configuration.

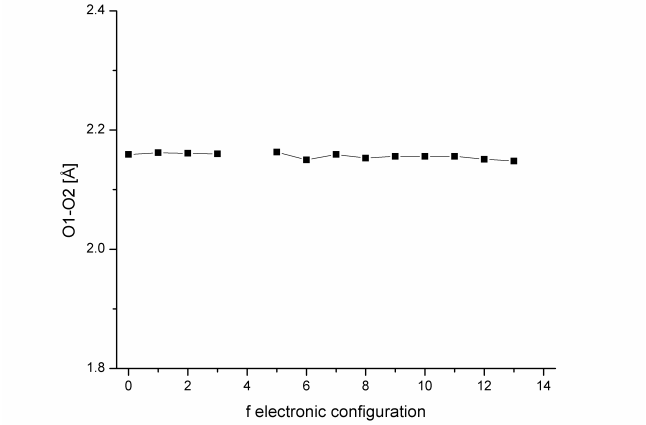



Figure S65. Distance O1-O2 vs. f electronic configuration.

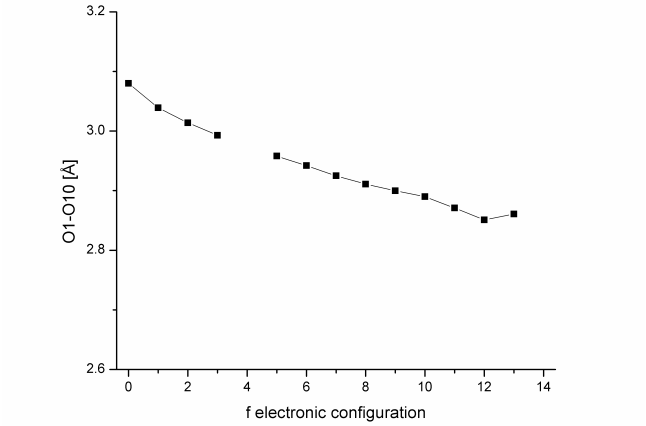



Figure S66. Distance O1-O10 vs. f electronic configuration.

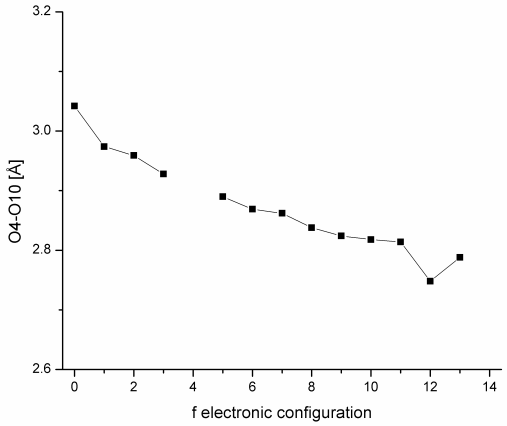



Figure S67. Distance O4-O10 vs. f electronic configuration.

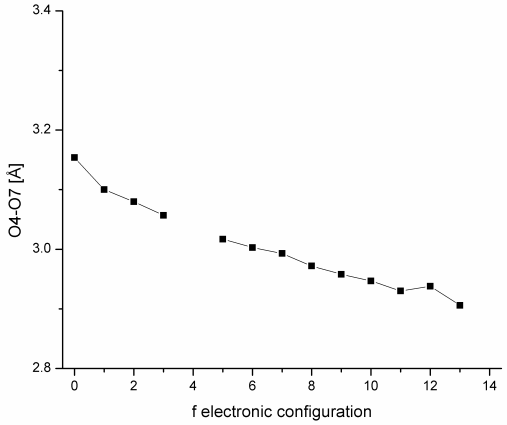



Figure S68. Distance O4-O7 vs. f electronic configuration.

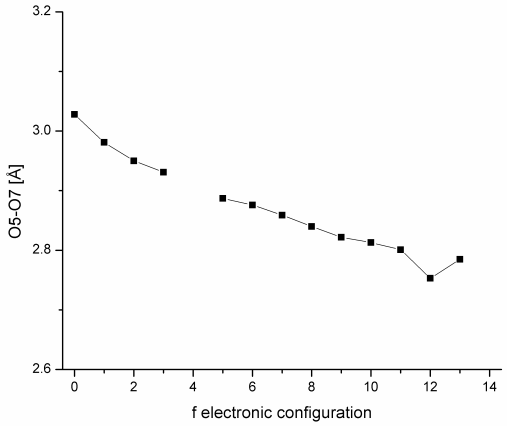



Figure S69. Distance O5-O7 vs. f electronic configuration.

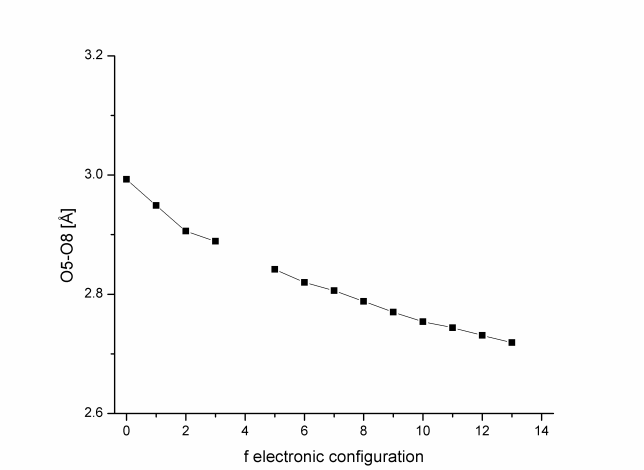



Figure S70. Distance O5-O8 vs. f electronic configuration.

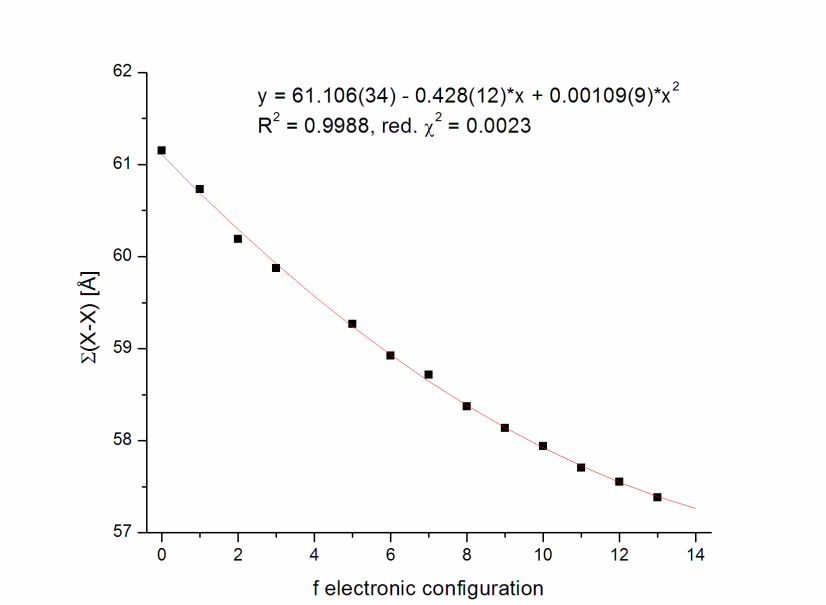
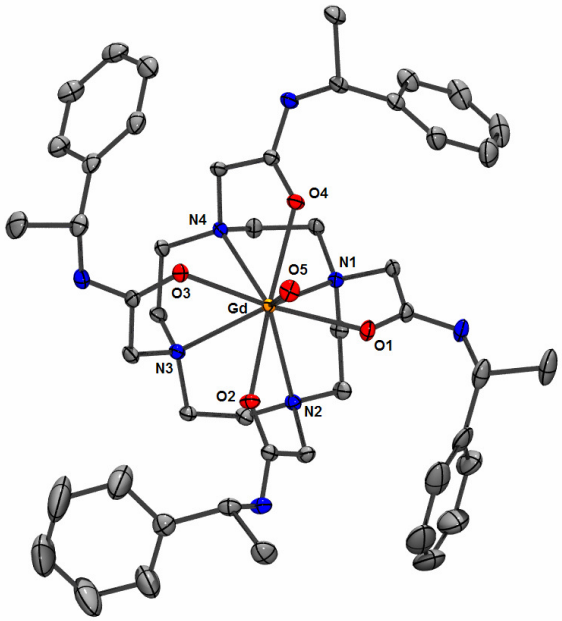



Figure S71. Sum of distance X-X (X = N, O) vs. f electronic configuration. Quadratic fit.

## 4. [Ln(PhMeCH-DOTAM)($H_2O$)] ($OTf)_3$ Complexes[9-11]

### 4.1 Structure




Asymmetric unit of [Ln(PhMeCH-DOTAM)($H_2O$)]($OTf)_3$ * 3 $H_2O$.[9] Thermal ellipsoid plot (Ortep 3 for Windows,[1] 50% probability level) with atom numbering scheme. Hydrogens, triflates, and the three isolated water molecules omitted for clarity.

### 4.2 Bond Lengths

Table S8. Bond lengths in [Ln(PhMeCH-DOTAM)($H_2O$)]($OTf)_3$ * 3 $H_2O$.[9-11]

| f electrons (Ln) | $d_{Ln-O1}$ (su) [Å] | $d_{Ln-O2}$ (su) [Å] | $d_{Ln-O3}$ (su) [Å] | $d_{Ln-O4}$ (su) [Å] | $d_{Ln-O5}$ (su) [Å] | $d_{Ln-N1}$ (su) [Å] | $d_{Ln-N2}$ (su) [Å] | $d_{Ln-N3}$ (su) [Å] | $d_{Ln-N4}$ (su) [Å] | $\Sigma d_{Ln-X}$ (su) [Å] |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | - | - | - | - | - | - | - | - | - | - |
| 1 (Ce) | - | - | - | - | - | - | - | - | - | - |
| 2 (Pr)[9] | 2.428(2) | 2.403(2) | 2.434(2) | 2.415(2) | 2.516(2) | 2.696(2) | 2.738(2) | 2.708(2) | 2.746(2) | 23.084(18) |
| 3 (Nd)[9] | 2.414(2) | 2.392(2) | 2.419(2) | 2.402(2) | 2.501(2) | 2.677(2) | 2.715(2) | 2.690(2) | 2.725(2) | 22.935(18) |
| 4 (Pm) | - | - | - | - | - | - | - | - | - | - |
| 5 (Sm)[9] | 2.374(4) | 2.352(4) | 2.383(4) | 2.362(4) | 2.495(2) | 2.647(5) | 2.685(5) | 2.654(5) | 2.697(5) | 22.649(40) |
| 6 (Eu)[9] | 2.377(2) | 2.355(2) | 2.379(2) | 2.361(2) | 2.482(2) | 2.643(2) | 2.680(2) | 2.655(2) | 2.689(2) | 22.621(18) |
| 7 (Gd)[9] | 2.368(2) | 2.346(2) | 2.367(2) | 2.353(2) | 2.460(2) | 2.633(2) | 2.670(2) | 2.650(2) | 2.675(2) | 22.522(18) |
| 8 (Tb)[10] | 2.355(2) | 2.333(2)* | 2.350(2)* | 2.331(2) | 2.461(3) | 2.624(3) | 2.664(3)* | 2.642(3)* | 2.669(3) | 22.429(23) |
| 9 (Dy)[9] | 2.344(2) | 2.315(2) | 2.336(2) | 2.317(2) | 2.454(2) | 2.620(2) | 2.654(2) | 2.644(2) | 2.658(2) | 22.342(18) |
| 10 (Ho) | - | - | - | - | - | - | - | - | - | - |
| 11 (Er)[10] | 2.321(1) | 2.296(2) | 2.310(1) | 2.294(2) | 2.432(2) | 2.605(2) | 2.639(2) | 2.629(2) | 2.636(2) | 22.162(15) |
| 12 (Tm) | - | - | - | - | - | - | - | - | - | - |
| 13 (Yb)[11] | 2.298(2)* | 2.274(2) | 2.288(2) | 2.274(2)* | 2.440(2) | 2.598(2) | 2.636(2) | 2.626(2) | 2.630(3) | 22.064(19) |
| 14 (Lu)[10] | 2.292(2) | 2.273(2) | 2.283(2) | 2.273(2) | 2.426(2) | 2.592(2) | 2.636(2) | 2.623(2) | 2.623(3) | 22.021(19) |
| $d_{Pr}$ / $d_{Lu}$ | 1.059 | 1.057 | 1.066 | 1.062 | 1.037 | 1.040 | 1.039 | 1.032 | 1.047 | 1.048 |

* Bond lengths taken from the published cif-files. Incorrectly listed in the original publication (see ref. 10 and 11).

## 4.3 X-X Distances

Table S9. Distances X-X (X = N,O bound to Ln) in [Ln(PhMeCH-DOTAM)($H_2O$)] ($OTf)_3$ * 3 $H_2O$.[9-11]

| f electrons (Ln) | $d_{O5-O1}$ [Å] | $d_{O5-O2}$ [Å] | $d_{O5-O3}$ [Å] | $d_{O5-O4}$ [Å] | $d_{O1-O2}$ [Å] | $d_{O2-O3}$ [Å] | $d_{O3-O4}$ [Å] | $d_{O4-O1}$ [Å] | $d_{O1-N1}$ [Å] | $d_{O1-N2}$ [Å] | $d_{O2-N2}$ [Å] | $d_{O2-N3}$ [Å] | $d_{O3-N3}$ [Å] | $d_{O3-N4}$ [Å] | $d_{O4-N4}$ [Å] | $d_{O4-N1}$ [Å] | $d_{N1-N2}$ [Å] | $d_{N2-N3}$ [Å] | $d_{N3-N4}$ [Å] | $d_{N4-N1}$ [Å] | $\Sigma d_{X-X}$ [Å] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 1 (Ce) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 2 (Pr)[9] | 2.909 | 2.984 | 3.015 | 2.989 | 3.259 | 3.310 | 3.222 | 3.372 | 2.794 | 3.086 | 2.729 | 3.037 | 2.785 | 3.096 | 2.763 | 3.114 | 2.999 | 3.019 | 2.990 | 3.025 | 60.497 |
| 3 (Nd)[9] | 2.883 | 2.955 | 2.967 | 2.953 | 3.236 | 3.276 | 3.209 | 3.337 | 2.791 | 3.067 | 2.725 | 3.018 | 2.779 | 3.082 | 2.764 | 3.087 | 2.988 | 3.009 | 2.979 | 3.013 | 60.118 |
| 4 (Pm) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 5 (Sm)[9] | 2.831 | 2.889 | 2.913 | 2.893 | 3.171 | 3.200 | 3.136 | 3.274 | 2.776 | 3.009 | 2.713 | 2.971 | 2.766 | 3.062 | 2.751 | 3.074 | 2.962 | 2.997 | 2.975 | 2.987 | 59.350 |
| 6 (Eu)[9] | 2.814 | 2.886 | 2.891 | 2.874 | 3.171 | 3.200 | 3.140 | 3.256 | 2.779 | 3.039 | 2.722 | 2.986 | 2.769 | 3.050 | 2.752 | 3.046 | 2.972 | 2.985 | 2.964 | 2.992 | 59.288 |
| 7 (Gd)[9] | 2.793 | 2.861 | 2.858 | 2.844 | 3.154 | 3.176 | 3.133 | 3.236 | 2.776 | 3.024 | 2.724 | 2.980 | 2.770 | 3.038 | 2.751 | 3.028 | 2.965 | 2.980 | 2.953 | 2.984 | 59.028 |
| 8 (Tb)[10] | 2.781 | 2.847 | 2.838 | 2.823 | 3.129 | 3.153 | 3.101 | 3.211 | 2.770 | 3.006 | 2.720 | 2.970 | 2.767 | 3.025 | 2.745 | 3.010 | 2.962 | 2.980 | 2.950 | 2.981 | 58.769 |
| 9 (Dy)[9] | 2.758 | 2.838 | 2.822 | 2.796 | 3.116 | 3.114 | 3.093 | 3.182 | 2.765 | 3.000 | 2.716 | 2.955 | 2.761 | 3.015 | 2.736 | 2.997 | 2.954 | 2.978 | 2.953 | 2.981 | 58.530 |
| 10 (Ho) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 11 (Er)[10] | 2.729 | 2.801 | 2.768 | 2.746 | 3.077 | 3.071 | 3.063 | 3.137 | 2.759 | 2.981 | 2.716 | 2.938 | 2.751 | 2.989 | 2.732 | 2.974 | 2.943 | 2.964 | 2.940 | 2.972 | 58.051 |
| 12 (Tm) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 13 (Yb)[11] | 2.715 | 2.797 | 2.758 | 2.727 | 3.038 | 3.035 | 3.037 | 3.111 | 2.750 | 2.959 | 2.717 | 2.926 | 2.745 | 2.972 | 2.725 | 2.956 | 2.933 | 2.963 | 2.935 | 2.974 | 57.773 |
| 14 (Lu)[10] | 2.704 | 2.777 | 2.736 | 2.710 | 3.032 | 3.022 | 3.033 | 3.101 | 2.747 | 2.954 | 2.727 | 2.921 | 2.742 | 2.963 | 2.733 | 2.953 | 2.930 | 2.966 | 2.931 | 2.974 | 57.656 |
| $d_{Pr}$ / $d_{Lu}$ | 1.076 | 1.075 | 1.102 | 1.103 | 1.075 | 1.095 | 1.062 | 1.087 | 1.017 | 1.045 | 1.001 | 1.040 | 1.016 | 1.045 | 1.011 | 1.055 | 1.024 | 1.018 | 1.020 | 1.017 | 1.049 |

## 4.4 Trends in Bond Lengths and X-X Distances vs. f Electron Configuration

Bond Lengths:

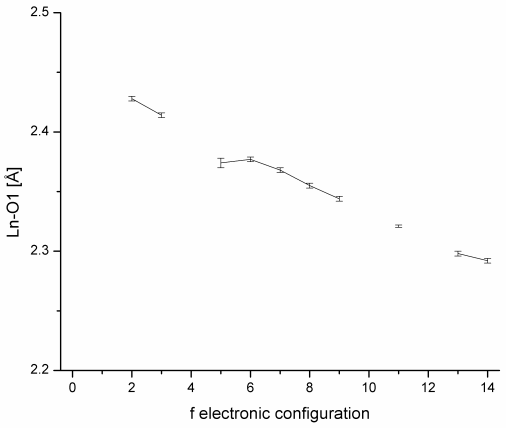



Figure S72. Bond length Ln-O1 vs. f electronic configuration.

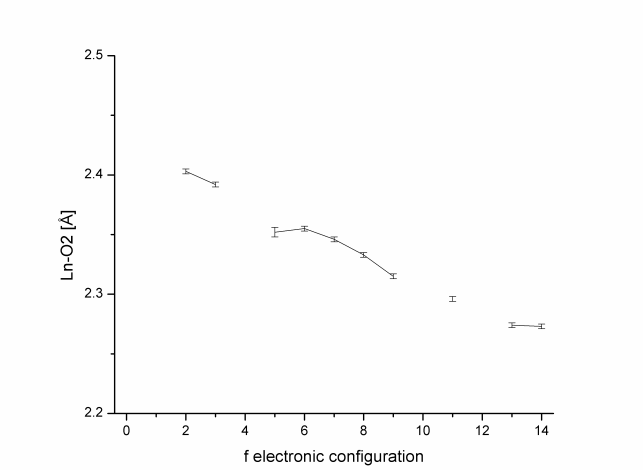



Figure S73. Bond length Ln-O2 vs. f electronic configuration.

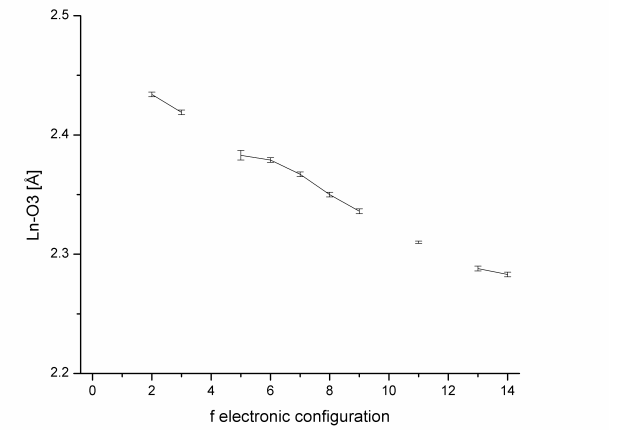



Figure S74. Bond length Ln-O3 vs. f electronic configuration.

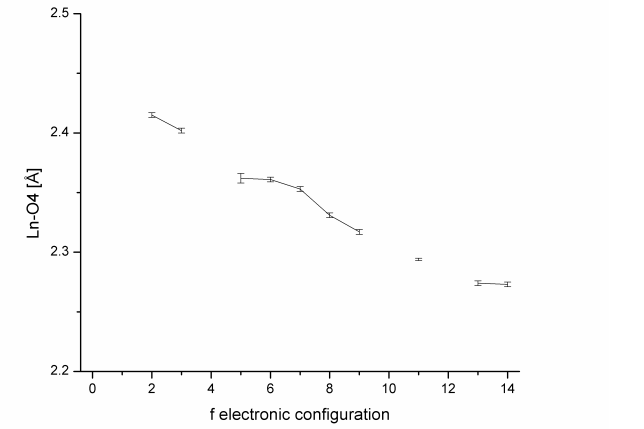



Figure S75. Bond length Ln-O4 vs. f electronic configuration.

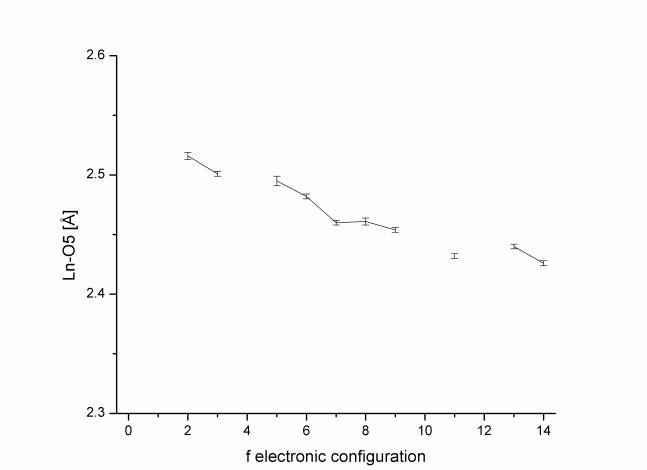



Figure S76. Bond length Ln-O5 vs. f electronic configuration.

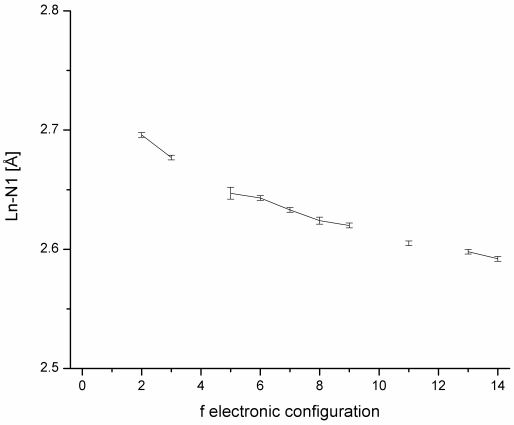



Figure S77. Bond length Ln-N1 vs. f electronic configuration.

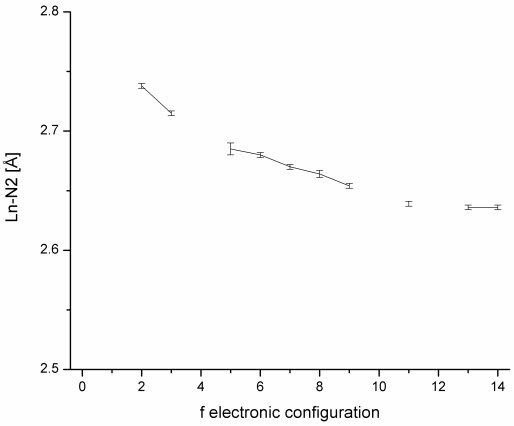



Figure S78. Bond length Ln-N2 vs. f electronic configuration.

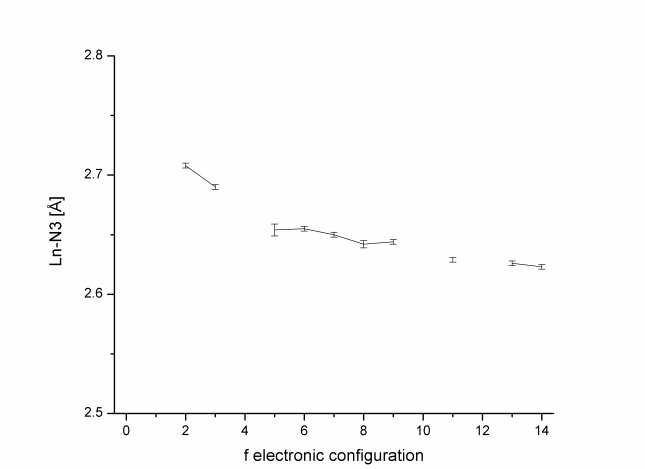



Figure S79. Bond length Ln-N3 vs. f electronic configuration.

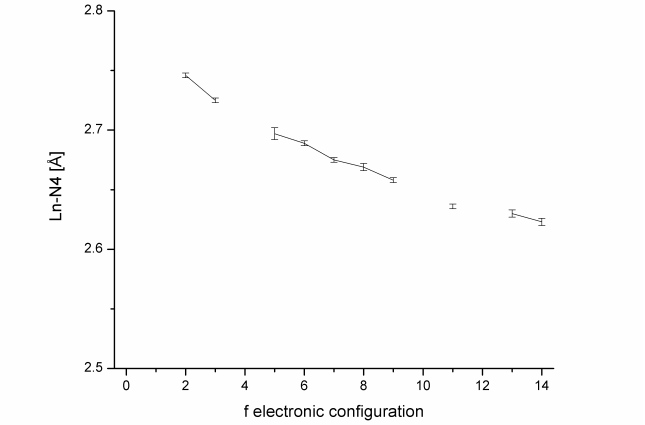



Figure S80. Bond length Ln-N4 vs. f electronic configuration.

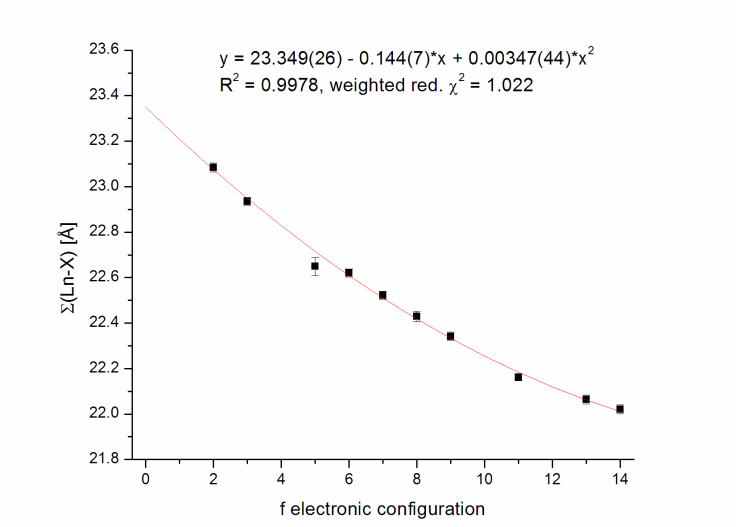



Figure S81. Sum of bond lengths Ln-X Ln-X (X = N, O) vs. f electronic configuration. Quadratic fit ($\chi^2$- weighting factor: $su^{-2}$).

Distances X-X (X = N,O):

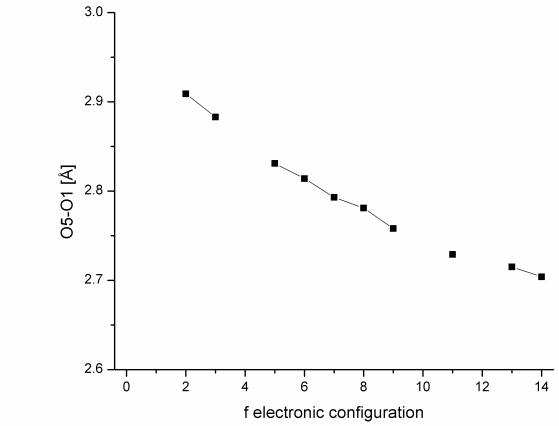



Figure S82. Distance O5-O1 vs. f electronic configuration.

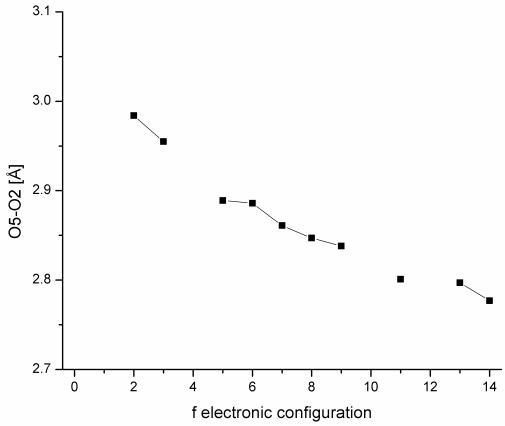



Figure S83. Distance O5-O2 vs. f electronic configuration.

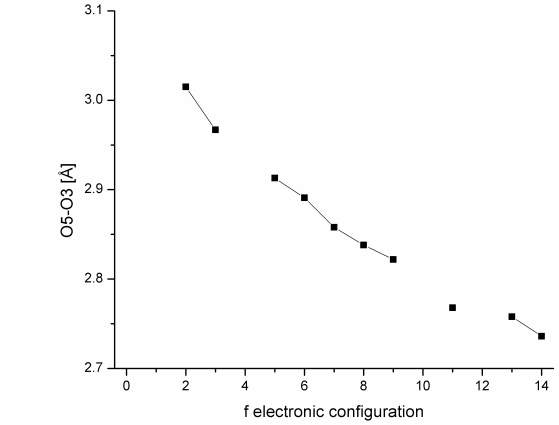



Figure S84. Distance O5-O3 vs. f electronic configuration.

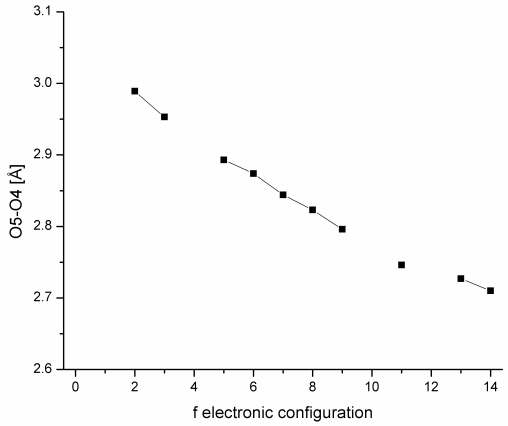



Figure S85. Distance O5-O4 vs. f electronic configuration.

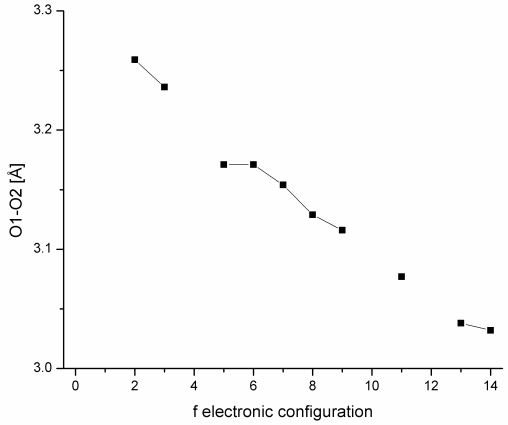



Figure S86. Distance O1-O2 vs. f electronic configuration.

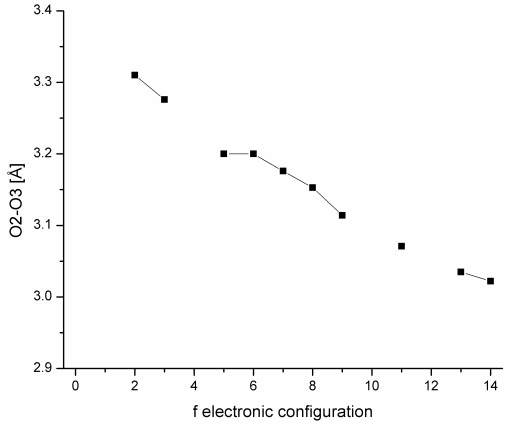



Figure S87. Distance O2-O3 vs. f electronic configuration.

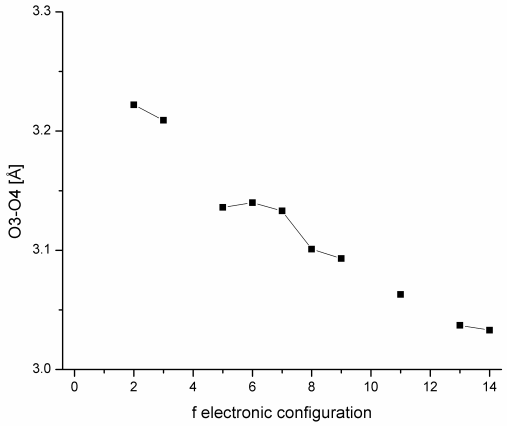



Figure S88. Distance O3-O4 vs. f electronic configuration.

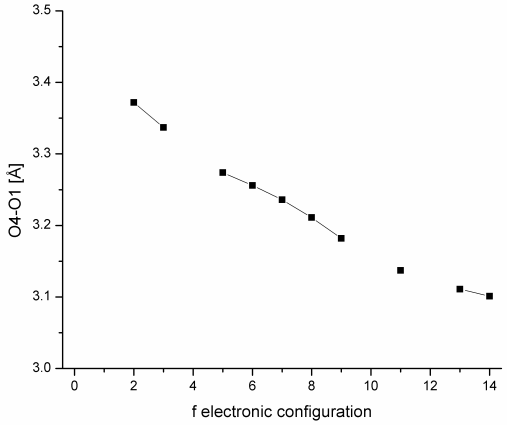



Figure S89. Distance O4-O1 vs. f electronic configuration.

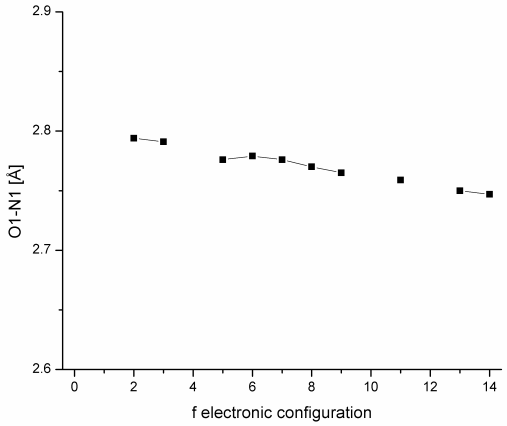



Figure S90. Distance O1-N1 vs. f electronic configuration.

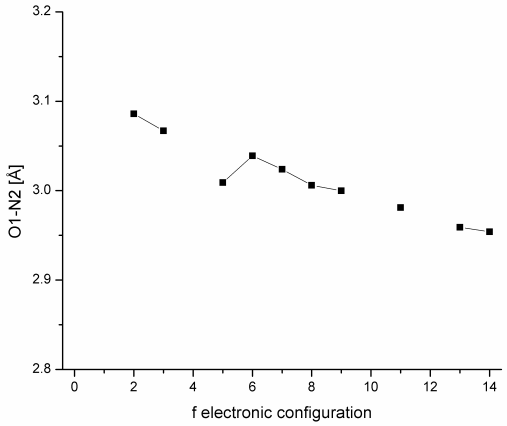



Figure S91. Distance O1-N2 vs. f electronic configuration.

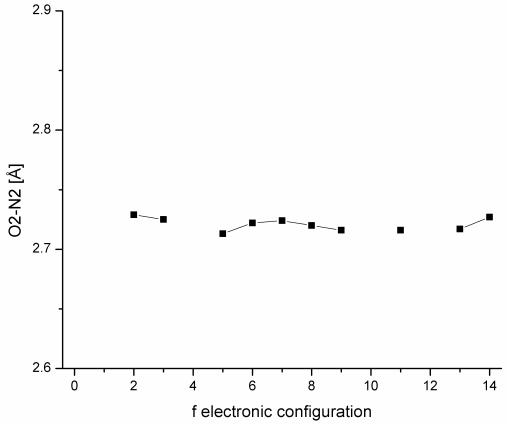



Figure S92. Distance O2-N2 vs. f electronic configuration.

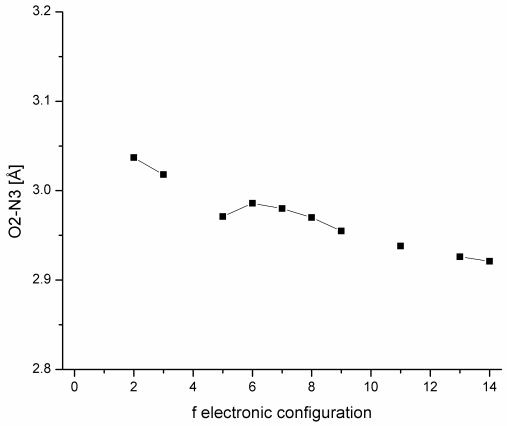



Figure S93. Distance O2-N3 vs. f electronic configuration.

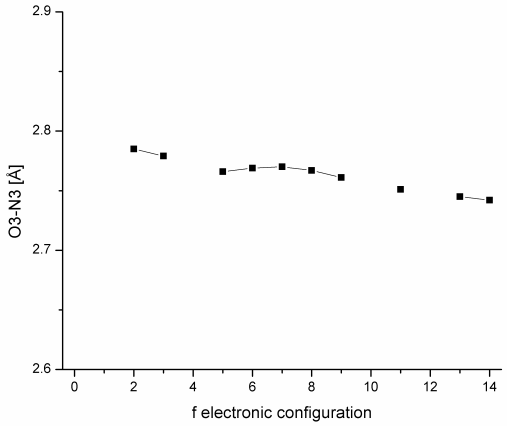



Figure S94. Distance O3-N3 vs. f electronic configuration.

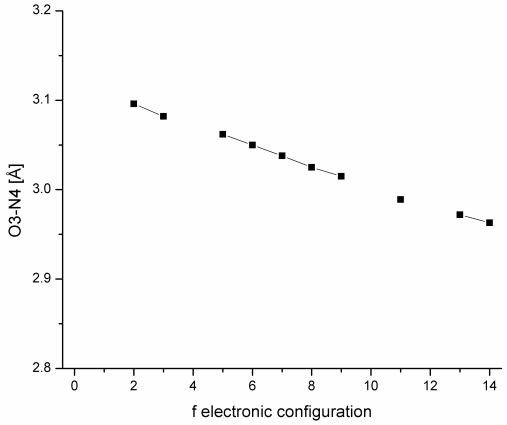



Figure S95. Distance O3-N4 vs. f electronic configuration.

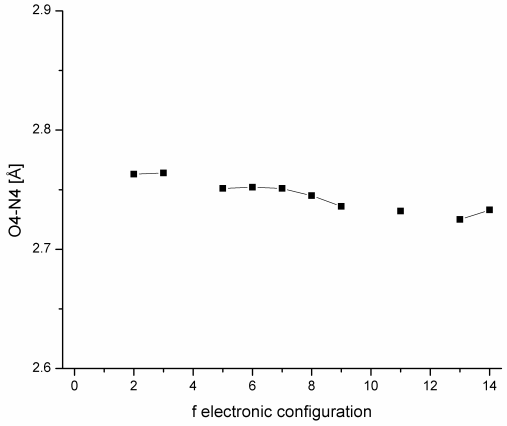



Figure S96. Distance O4-N4 vs. f electronic configuration.

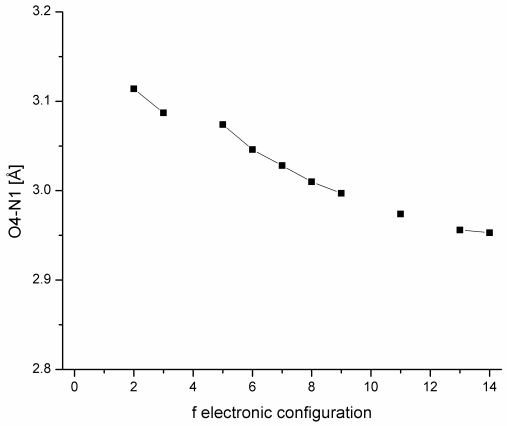



Figure S97. Distance O4-N1 vs. f electronic configuration.

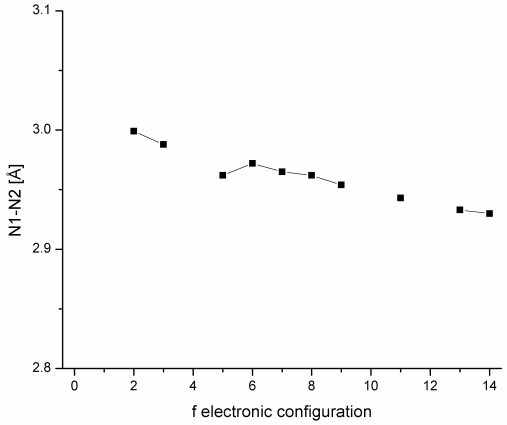



Figure S98. Distance N1-N2 vs. f electronic configuration.

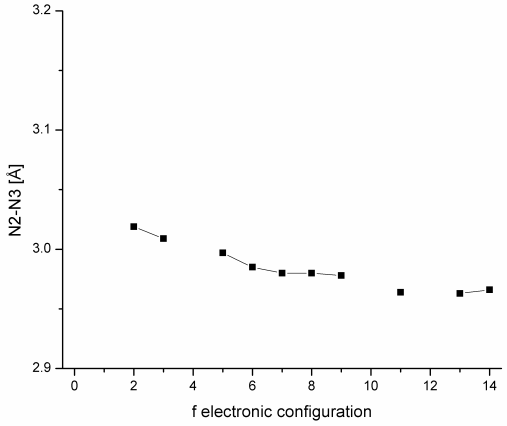



Figure S99. Distance N2-N3 vs. f electronic configuration.

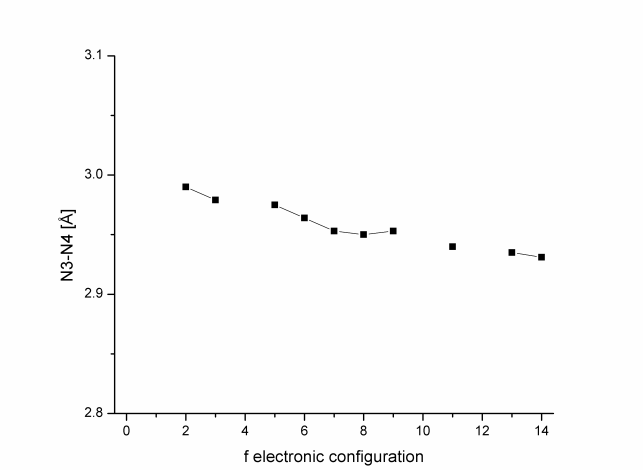



Figure S100. Distance N3-N4 vs. f electronic configuration.

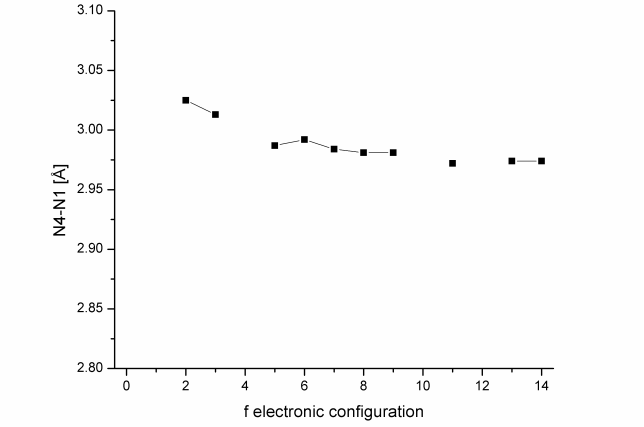



Figure S101. Distance N4-N1 vs. f electronic configuration.

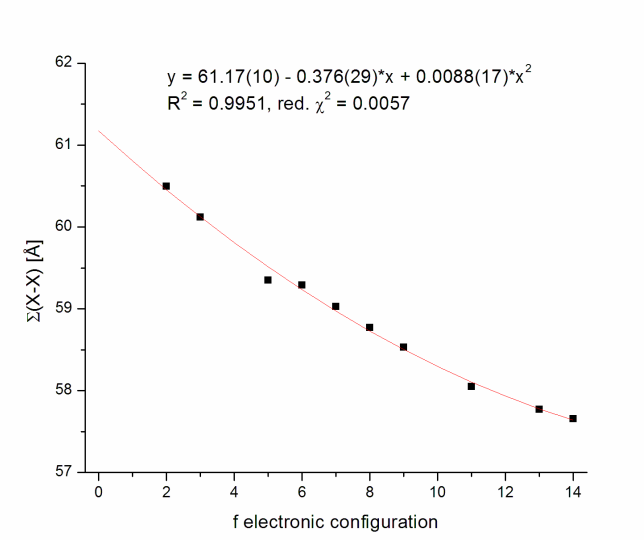



Figure S102. Sum of distance X-X (X = N, O) vs. f electronic configuration. Quadratic fit.

# 5 $[Ln(H_2O)_9](EtOSO_3)_3$ Complexes[12]

## 5.1 Bond Lengths

Table S10. Bond lengths in $[Ln(H_2O)_9](EtOSO_3)_3$.[12]

| f electrons (Ln) | $d_{Ln-O1}$ (su) [Å] (6x) | $d_{Ln-O2}$ (su) [Å] (3x) | $\Sigma d_{Ln-O}$ (su) [Å] |
|---|---|---|---|
| 0 (La) | 2.517(1) | 2.616(3) | 22.950(15) |
| 1 (Ce) | 2.491(1) | 2.600(3) | 22.746(15) |
| 2 (Pr) | 2.470(2) | 2.583(3) | 22.569(21) |
| 3 (Nd) | 2.457(1) | 2.570(2) | 22.452(12) |
| 4 (Pm) | - | - | |
| 5 (Sm) | 2.430(1) | 2.550(4) | 22.230(18) |
| 6 (Eu) | 2.415(1) | 2.542(3) | 22.116(15) |
| 7 (Gd) | 2.401(1) | 2.536(3) | 22.014(15) |
| 8 (Tb) | 2.382(2) | 2.527(3) | 21.873(21) |
| 9 (Dy) | 2.371(1) | 2.517(4) | 21.777(15) |
| 10 (Ho) | 2.362(2) | 2.511(4) | 21.705(24) |
| 11 (Er) | 2.352(2) | 2.503(3) | 21.621(21) |
| 12 (Tm) | 2.340(2) | 2.504(5) | 21.552(27) |
| 13 (Yb) | 2.324(2) | 2.503(3) | 21.453(21) |
| 14 (Lu) | 2.318(2) | 2.497(3) | 21.399(21) |
| $d_{La}$ / $d_{Lu}$ | 1.086 | 1.048 | 1.072 |

## 5.2 O-O Distances

Table S11. Distances O-O (O bound to Ln) in $[Ln(H_2O)_9](EtOSO_3)_3$.[12]

| f electrons (Ln) | $d_{O1'-O2}$ [Å] (6x) | $d_{O1-O2}$ [Å] (6x) | $d_{O1-O1'}$ [Å] (3x) | $d_{O1'-O1'}$ [Å] (6x)* | $\Sigma d_{O-O}$ [Å] |
|---|---|---|---|---|---|
| 0 (La) | 2.770 | 3.058 | 3.531 | 3.108 | 64.209 |
| 1 (Ce) | 2.753 | 3.034 | 3.509 | 3.062 | 63.621 |
| 2 (Pr) | 2.735 | 3.009 | 3.483 | 3.033 | 63.111 |
| 3 (Nd) | 2.726 | 2.995 | 3.475 | 3.010 | 62.811 |
| 4 (Pm) | - | - | - | - | - |
| 5 (Sm) | 2.704 | 2.966 | 3.444 | 2.969 | 62.166 |
| 6 (Eu) | 2.695 | 2.952 | 3.428 | 2.948 | 61.854 |
| 7 (Gd) | 2.683 | 2.940 | 3.402 | 2.935 | 61.554 |
| 8 (Tb) | 2.673 | 2.920 | 3.379 | 2.909 | 61.149 |
| 9 (Dy) | 2.661 | 2.909 | 3.369 | 2.890 | 60.867 |
| 10 (Ho) | 2.654 | 2.901 | 3.357 | 2.878 | 60.669 |
| 11 (Er) | 2.649 | 2.884 | 3.339 | 2.868 | 60.423 |
| 12 (Tm) | 2.648 | 2.875 | 3.325 | 2.853 | 60.231 |
| 13 (Yb) | 2.638 | 2.865 | 3.300 | 2.833 | 59.916 |
| 14 (Lu) | 2.633 | 2.854 | 3.285 | 2.832 | 59.769 |
| $d_{La}$ / $d_{Lu}$ | 1.052 | 1.071 | 1.075 | 1.097 | 1.074 |

* Distance not listed in the original publication; values calculated from the published coordinates (see ref. 12).

## 5.3 Trends in Bond Lengths and O-O Distances vs. f Electron Configuration

Bond Lengths:

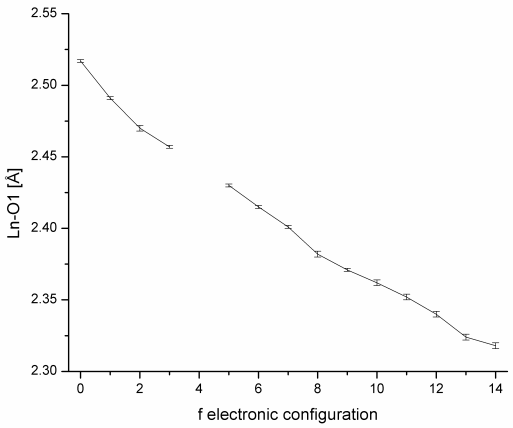



Figure S103. Bond length Ln-O1 vs. f electronic configuration.

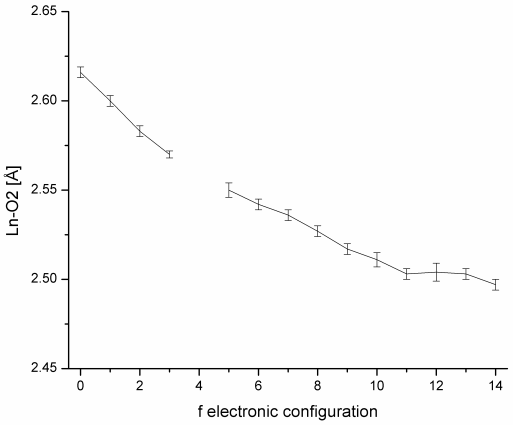



Figure S104. Bond length Ln-O2 vs. f electronic configuration.

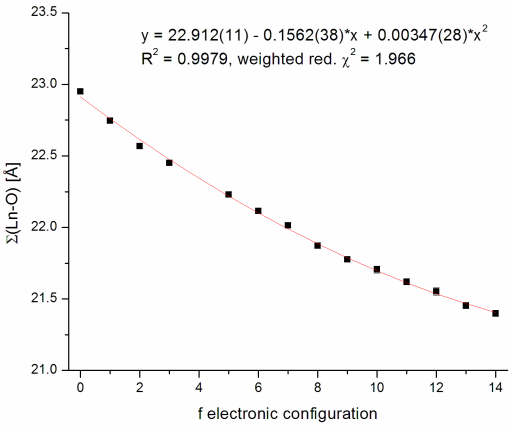



Figure S105. Sum of bond lengths Ln-O vs. f electronic configuration. Quadratic fit ($\chi^2$- weighting factor: $su^{-2}$).

Distances O-O:

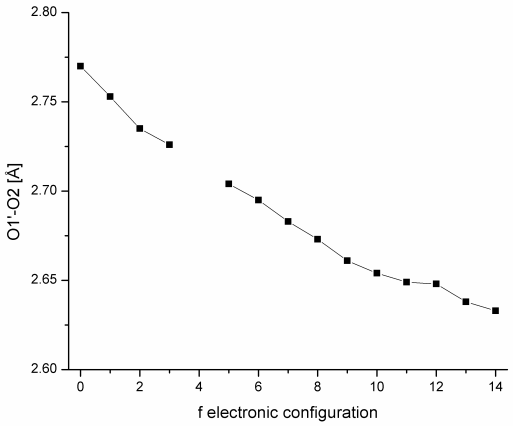



Figure S106. Distance O1'-O2 vs. f electronic configuration.

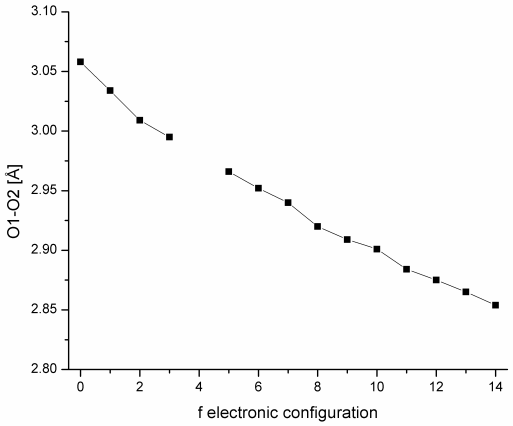



Figure S107. Distance O1-O2 vs. f electronic configuration.

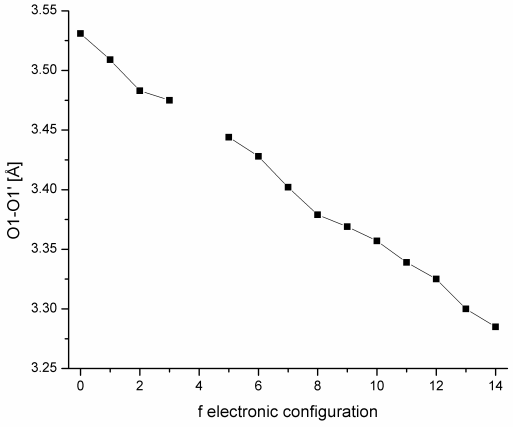



Figure S108. Distance O1-O1' vs. f electronic configuration.

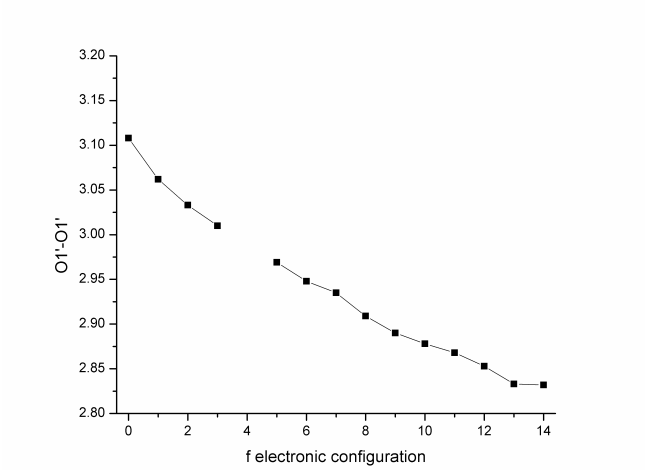



Figure S109. Distance O1'-O1' vs. f electronic configuration.

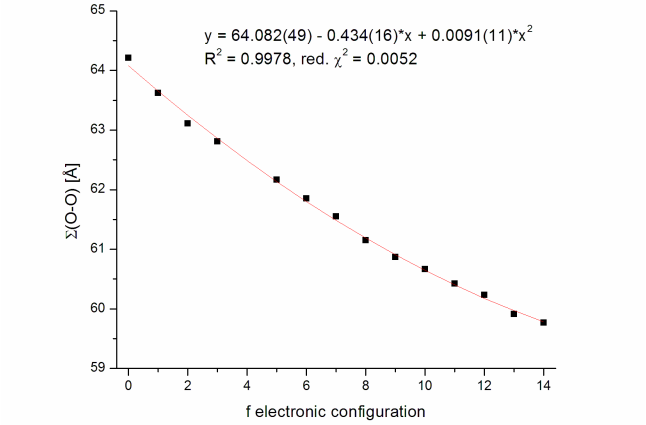



Figure S110. Sum of distances O-O vs. f electronic configuration. Quadratic fit ($\chi^2$- weighting factor: $su^{-2}$).

## 6. The Average X-X Distance vs. the Average Ln-X Bond Length

Table S12. Average distances Ln-X and X-X (X=N,O; bound to Ln).

| f electrons (Ln) | [Ln(TREN-1,2-HOIQO)($H_2O$)] avg. Ln-O [Å] | [Ln(TREN-1,2-HOIQO)($H_2O$)] avg. O-O [Å] | [Ln(tptz)($NO_3$)$_3$($H_2O$)] avg. Ln-X [Å] | [Ln(tptz)($NO_3$)$_3$($H_2O$)] avg. X-X [Å] | [Ln((PhMeCH-DOTAM)($H_2O$)](OTf)$_3$ avg. Ln-X [Å] | [Ln((PhMeCH-DOTAM)($H_2O$)](OTf)$_3$ avg. X-X [Å] | [Ln($H_2O$)$_9$](EtOSO$_3$)$_3$ avg. Ln-O [Å] | [Ln($H_2O$)$_9$](EtOSO$_3$)$_3$ avg. O-O [Å] | [Ln(TREN-SAL)] avg. Ln-X [Å] | [Ln(TREN-SAL)] avg. X-X [Å] |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 (La) | 2.486 | 3.152 | 2.615 | 2.912 | - | - | 2.550 | 3.058 | - | - |
| 1 (Ce) | 2.465 | 3.125 | 2.598 | 2.892 | - | - | 2.527 | 3.030 | 2.576 | 3.344 |
| 2 (Pr) | 2.448 | 3.104 | 2.575 | 2.866 | 2.565 | 3.025 | 2.508 | 3.005 | 2.558 | 3.322 |
| 3 (Nd) | 2.431 | 3.083 | 2.562 | 2.851 | 2.548 | 3.006 | 2.495 | 2.991 | 2.547 | 3.316 |
| 4 (Pm) | - | - | - | - | - | - | - | - | - | - |
| 5 (Sm) | 2.407 | 3.050 | 2.536 | 2.822 | 2.517 | 2.968 | 2.470 | 2.960 | 2.517 | 3.272 |
| 6 (Eu) | 2.393 | 3.033 | 2.521 | 2.806 | 2.513 | 2.964 | 2.457 | 2.945 | 2.510 | 3.264 |
| 7 (Gd) | 2.381 | 3.017 | 2.513 | 2.796 | 2.502 | 2.951 | 2.446 | 2.931 | 2.496 | 3.250 |
| 8 (Tb) | 2.362 | 2.993 | 2.498 | 2.780 | 2.492 | 2.938 | 2.430 | 2.912 | 2.478 | 3.223 |
| 9 (Dy) | 2.355 | 2.984 | 2.488 | 2.769 | 2.482 | 2.927 | 2.420 | 2.898 | 2.473 | 3.212 |
| 10 (Ho) | 2.340 | 2.965 | 2.480 | 2.759 | - | - | 2.412 | 2.889 | 2.456 | 3.198 |
| 11 (Er) | 2.334 | 2.957 | 2.470 | 2.748 | 2.462 | 2.903 | 2.402 | 2.877 | - | - |
| 12 (Tm) | 2.324 | 2.947 | 2.465 | 2.741 | - | - | 2.395 | 2.868 | - | - |
| 13 (Yb) | 2.310 | 2.925 | 2.455 | 2.733 | 2.452 | 2.889 | 2.384 | 2.853 | 2.428 | 3.154 |
| 14 (Lu) | 2.314 | 2.929 | - | - | 2.447 | 2.883 | 2.378 | 2.846 | - | - |

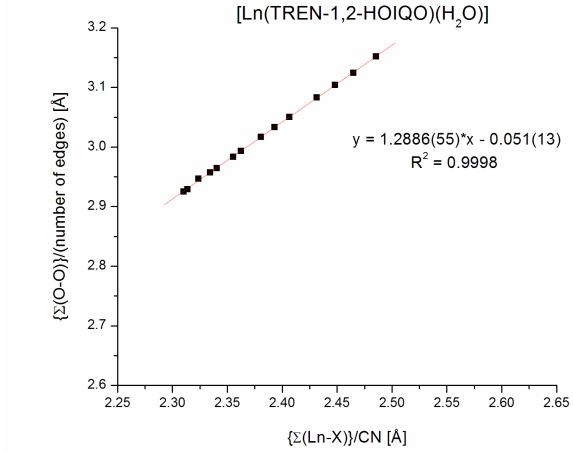



Figure S111. Average O-O vs. average Ln-O in [Ln(TREN-1,2-HOIQO)($H_2O$)].

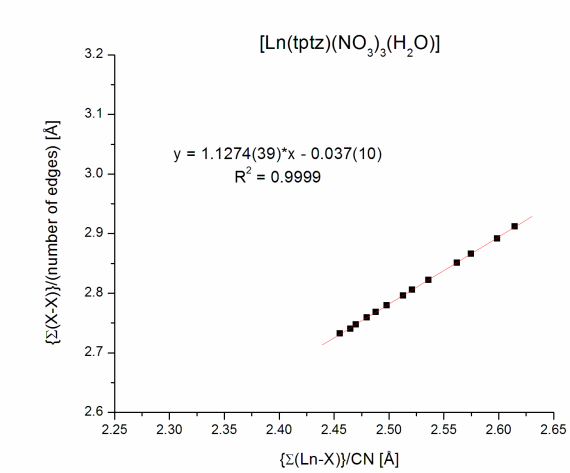



Figure S112. Average O-O vs. average Ln-O in [Ln(tptz)($NO_3$)$_3$($H_2O$)].

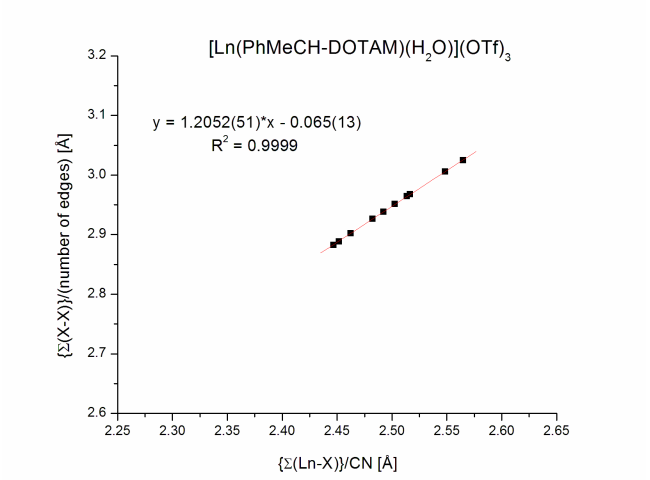



Figure S113. Average O-O vs. average Ln-O in [Ln(PhMeCH-DOTAM)$(H_2O)$]$(OTf)_3$.

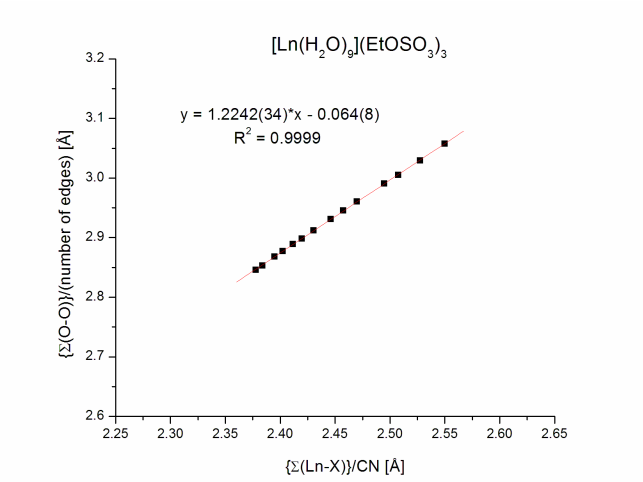



Figure S114. Average O-O vs. average Ln-O in $[Ln(H_2O)_9](EtOSO_3)_3$.

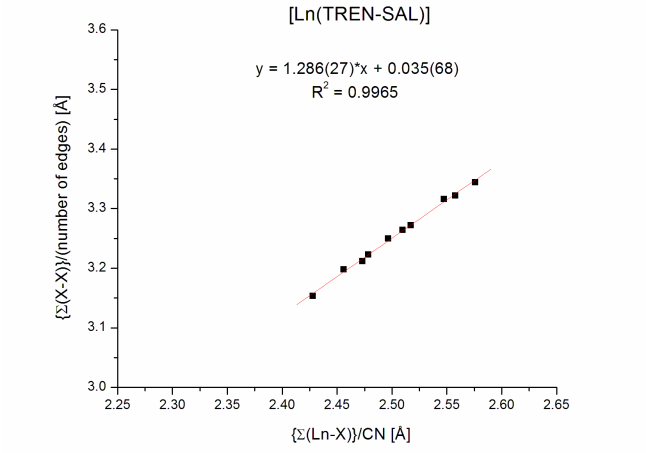



Figure S115. Average X-X vs. average Ln-X in [Ln(TREN-SAL)].

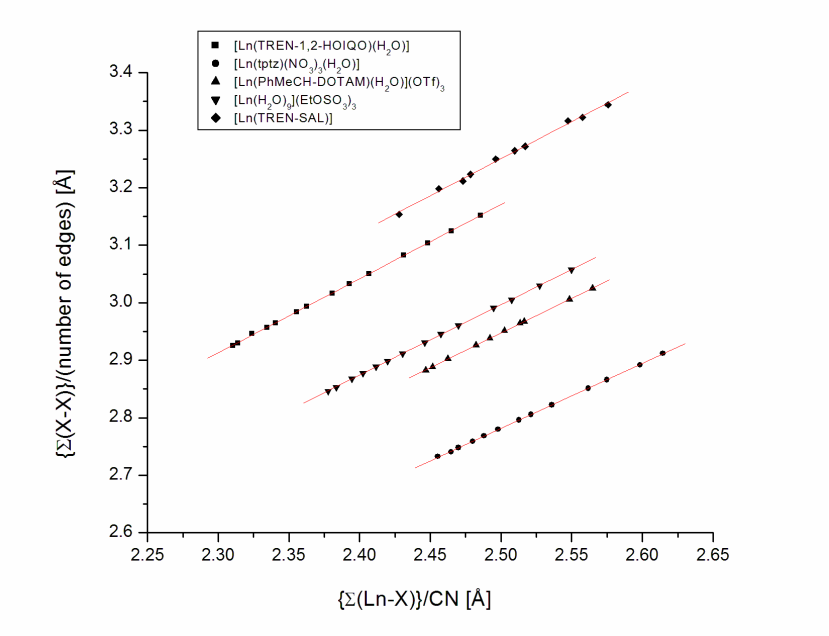



Figure S116. Average X-X vs. average Ln-X in all complexes.

## 7. References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