# Understanding the Scarcity of Thorium Peroxide Clusters

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## Supporting Information

## Crystallographic data

**Table S1.** Crystallographic table of $[Th(O_2)(terpy)(NO_3)_2]_3{\cdot}3CH_3CN$.

| Compound | $[Th(O_2)(terpy)(NO_3)_2]_3{\cdot}3CH_3CN$ |
|---|---|
| Formula Mass | 1987.14 |
| Color and habit | Colorless, tablet |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 13.2177(12) |
| $b$ (Å) | 13.9068(13) |
| $c$ (Å) | 18.4265(17) |
| $\alpha$(°) | 86.9880(15) |
| $\beta$ (°) | 88.0749(15) |
| $\gamma$ (°) | 83.8940(16) |
| $V$ (Å$^3$) | 3361.9(5) |
| Z | 2 |
| $T$ (K) | 100 (2) |
| $\lambda$ (Å) | 0.71073 |
| Maximum 2θ (°) | 56.222 |
| $\rho_{calc}$ (g/cm$^3$) | 1.963 |
| $\mu$ (Mo $K\alpha$) (cm$^{-1}$) | 67.07 |
| $R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$ | 0.0313 |
| $R_w(F_o^2)^b$ | 0.0987 |

**Table S2.** Selected Bond Lengths for $[Th(O_2)(terpy)(NO_3)_2]_3$ (Å).

| Th-Terpy | | Th-Nitrate | | Th-Peroxide | |
|---|---|---|---|---|---|
| Th(1)-N(1) | 2.693(5) | Th(1)-O(2) | 2.551(4) | Th(1)-O(19) | 2.332(4) |
| Th(1)-N(2) | 2.717(4) | Th(1)-O(3) | 2.664(4) | Th(1)-O(20) | 2.387(4) |
| Th(1)-N(3) | 2.711(4) | Th(1)-O(5) | 2.598(4) | Th(1)-O(23) | 2.367(4) |
| Th(2)-N(4) | 2.671(5) | Th(1)-O(6) | 2.596(4) | Th(1)-O(24) | 2.408(4) |
| Th(2)-N(5) | 2.701(4) | Th(2)-O(8) | 2.566(4) | Th(2)-O(21) | 2.339(4) |
| Th(2)-N(6) | 2.742(5) | Th(2)-O(9) | 2.742(4) | Th(2)-O(22) | 2.406(4) |
| Th(3)-N(7) | 2.642(5) | Th(2)-O(10) | 2.642(4) | Th(2)-O(23) | 2.353(4) |
| Th(3)-N(8) | 2.681(5) | Th(2)-O(11) | 2.647(4) | Th(2)-O(24) | 2.366(4) |
| Th(3)-N(9) | 2.668(5) | Th(3)-O(14) | 2.581(4) | Th(3)-O(19) | 2.366(4) |
| | | Th(3)-O(15) | 2.633(4) | Th(3)-O(20) | 2.371(4) |
| | | Th(3)-O(17) | 2.609(4) | Th(3)-O(21) | 2.337(4) |
| | | Th(3)-O(18) | 2.599(4) | Th(3)-O(22) | 2.398(4) |

## Computational details

All the structures reported in this study were fully optimized with the Becke's 3-parameter hybrid functional[14] combined with the non-local correlation functional provided by Perdew/Wang[15] (denoted as B3PW91). The thorium atom was represented by relativistic energy-consistent small-core pseudopotential obtained from the Stuttgart-Köln ECP library has been used in combination with its adapted segmented basis set.[16] Large-core calculations were also used to probe the oxidation state of the thorium in the trimer.[16,17] For the remaining atoms the 6-31G(d,p) basis set was used.[18,19] In all computations no constraints were imposed on the geometry. All stationary points have been identified as minima (number of imaginary frequencies Nimag=0) or transition states (Nimag=1). The vibrational modes and the corresponding frequencies are based on a harmonic force field. Enthalpy energies were obtained at T=298.15K within the harmonic approximation. GAUSSIAN09 program suite was used in all calculations.[20] Finally, for the 3D representation of the structures the Chemcraft[21] program was used as well as for the visualization of the molecular orbitals.

Cartesian coordinates of the optimized structure of the trimer

| | | | |
|---|---|---|---|
| Th | 4.16144 | 9.33665 | 6.81882 |
| Th | 4.06733 | 12.33558 | 3.69412 |
| Th | 7.05563 | 9.33975 | 3.78194 |
| O | 5.65633 | 13.86911 | 2.11622 |
| O | 3.54879 | 11.26615 | 8.47016 |
| O | 7.90321 | 6.99235 | 4.53116 |
| O | 5.51883 | 10.41616 | 8.67854 |
| O | 3.25267 | 6.94425 | 6.73449 |
| O | 9.15559 | 9.47427 | 5.22159 |
| O | 2.71884 | 8.15650 | 5.03456 |
| O | 1.48544 | 12.67985 | 3.65621 |
| O | 2.12893 | 10.75104 | 2.94613 |
| O | 7.95987 | 11.26549 | 5.17005 |
| O | 8.79447 | 7.84308 | 2.76312 |
| N | 3.12700 | 14.73742 | 2.79748 |

| | | | |
|---|---|---|---|
| N | 5.80032 | 7.37159 | 2.43857 |
| O | 9.49638 | 5.91366 | 3.50246 |
| N | 3.17932 | 8.52894 | 9.23542 |
| N | 1.53242 | 9.52894 | 7.33571 |
| O | 5.83502 | 14.03259 | 4.25914 |
| N | 8.92221 | 10.78528 | 2.31899 |
| O | -0.00158 | 11.15576 | 3.18059 |
| N | 3.31659 | 14.21046 | 5.45386 |
| N | 5.54977 | 7.53882 | 8.32039 |
| O | 2.19209 | 6.03980 | 5.05595 |
| N | 6.95721 | 9.40846 | 1.03877 |
| N | 3.37586 | 12.56949 | 1.14621 |
| N | 8.92854 | 10.63841 | 5.71274 |
| N | 2.69674 | 7.00875 | 5.58457 |
| N | 8.76440 | 6.87120 | 3.60304 |
| O | 4.94731 | 12.13226 | 9.90073 |
| O | 9.60501 | 11.11009 | 6.59655 |
| N | 4.68731 | 11.30882 | 9.05124 |
| N | 6.27222 | 14.37420 | 3.10156 |
| O | 7.20335 | 15.14260 | 2.97301 |
| N | 1.16053 | 11.51445 | 3.25487 |
| C | 5.21849 | 7.28973 | 9.59899 |
| C | 0.71332 | 9.87846 | 6.33803 |
| H | 1.14746 | 9.87589 | 5.34548 |
| C | 1.99628 | 9.02319 | 9.64541 |
| C | 3.74080 | 8.00951 | 11.50334 |
| H | 4.45281 | 7.61942 | 12.21967 |
| C | 1.05352 | 9.47379 | 8.59059 |
| C | 6.16962 | 8.55662 | 0.36340 |
| C | 6.59692 | 6.89919 | 7.78770 |
| H | 6.83369 | 7.14697 | 6.76063 |
| C | 4.01537 | 7.97562 | 10.13088 |
| C | 4.95522 | 6.35281 | 0.44847 |
| H | 4.84928 | 6.35182 | -0.62924 |
| C | 5.87619 | 8.75087 | -0.99241 |
| H | 5.22436 | 8.07041 | -1.52515 |
| C | 5.62203 | 7.39217 | 1.10501 |
| C | 7.36641 | 5.98406 | 8.50294 |
| H | 8.20508 | 5.49867 | 8.01608 |
| C | 7.26690 | 10.69460 | -0.95616 |
| H | 7.74368 | 11.52175 | -1.46606 |
| C | 8.47594 | 11.29018 | 1.15510 |
| C | 6.43139 | 9.83629 | -1.65299 |
| H | 6.22755 | 10.00226 | -2.70675 |
| C | 7.50737 | 10.45501 | 0.40201 |
| C | -1.12708 | 10.15474 | 7.82972 |
| H | -2.16638 | 10.39563 | 8.03394 |
| C | -0.28308 | 9.77508 | 8.86845 |
| H | -0.67324 | 9.70120 | 9.87627 |
| C | -0.62432 | 10.20722 | 6.53600 |
| H | -1.23098 | 10.49519 | 5.68494 |
| C | 4.43315 | 5.29683 | 1.18649 |
| H | 3.90502 | 4.49020 | 0.68669 |
| C | 2.97896 | 13.73284 | 0.60208 |
| C | 7.03047 | 5.72284 | 9.82372 |
| H | 7.59980 | 5.01264 | 10.41634 |
| C | 1.65696 | 9.07247 | 11.00065 |
| H | 0.72125 | 9.51003 | 11.32453 |
| C | 5.93826 | 6.38066 | 10.37936 |
| H | 5.63980 | 6.16431 | 11.39815 |

| | | | |
|---|---|---|---|
| C | 5.30402 | 6.34694 | 3.14269 |
| H | 5.47960 | 6.38962 | 4.21115 |
| C | 10.54106 | 12.55313 | 2.44514 |
| H | 11.37121 | 12.99891 | 2.98173 |
| C | 3.07516 | 15.48509 | 5.09345 |
| C | 10.00346 | 13.14142 | 1.30814 |
| H | 10.38416 | 14.08726 | 0.93545 |
| C | 2.99073 | 14.93469 | 1.47471 |
| C | 8.97062 | 12.49224 | 0.64232 |
| H | 8.54275 | 12.93575 | -0.24825 |
| C | 2.53855 | 13.79039 | -0.72451 |
| H | 2.17074 | 14.71714 | -1.14767 |
| C | 9.95433 | 11.38399 | 2.92019 |
| H | 10.32898 | 10.89677 | 3.81298 |
| C | 2.55687 | 8.58504 | 11.93767 |
| H | 2.33258 | 8.64679 | 12.99827 |
| C | 3.32667 | 13.89324 | 6.75155 |
| H | 3.52514 | 12.85583 | 6.98725 |
| C | 4.60052 | 5.29523 | 2.56383 |
| H | 4.19660 | 4.50940 | 3.19139 |
| C | 2.98324 | 11.44480 | -0.92897 |
| H | 3.00075 | 10.51802 | -1.49118 |
| C | 3.04727 | 15.78103 | 3.63898 |
| C | 3.38658 | 11.45850 | 0.40216 |
| H | 3.72777 | 10.56259 | 0.91301 |
| C | 2.85119 | 16.21617 | 0.93603 |
| H | 2.79036 | 16.36746 | -0.13434 |
| C | 2.54071 | 12.63413 | -1.49563 |
| H | 2.19096 | 12.66536 | -2.52352 |
| C | 3.10615 | 14.82642 | 7.76242 |
| H | 3.14934 | 14.50195 | 8.79616 |
| C | 2.85162 | 16.14082 | 7.40113 |
| H | 2.67066 | 16.90413 | 8.15245 |
| C | 2.82806 | 16.47319 | 6.04981 |
| H | 2.60985 | 17.49264 | 5.75646 |
| C | 2.91573 | 17.09172 | 3.16005 |
| H | 2.89831 | 17.93316 | 3.84037 |
| O | 5.46263 | 8.31286 | 5.19758 |
| O | 6.38999 | 9.12842 | 6.02509 |
| O | 3.25738 | 11.10060 | 5.52360 |
| O | 6.06828 | 11.30956 | 2.99764 |
| O | 4.69646 | 11.41756 | 5.77684 |
| O | 4.98561 | 10.28609 | 2.95431 |
| C | 2.83456 | 17.30676 | 1.79428 |
| H | 2.75584 | 18.31547 | 1.40041 |