Electronic Supplementary information

Exafs and DFT : Evidence for the $[Tc{=}O]^{2+}$ core

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S1: overview of the EXAFS data analysis and modelling algorithm

Data reduction and analysis were achieved using a combination of XAS and modelling tools including EXAFSPAK, IFEFFIT, FEFF8, Gaussian03[1] (**Fig. S1**). The raw data for each sample was first recalibrated and different scans were averaged using the mcalib and mave tools from the exafspak suite of programs.[2] The resulting data were imported into ATHENA for data reduction purposes such as background subtraction using the autobk algorithm and normalization of the edge jump. Fitting the normalized EXAFS signal was performed in the IFEFFIT fitting module ARTEMIS.[3] All fitting was done in k-space using an overall scaling factor S_0^2 fixed at 1.

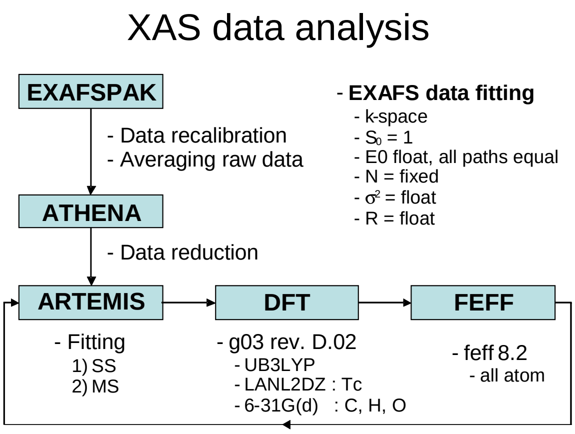

Fig. S1 Schematic representation of EXAFS data analysis and modelling algorithm

S2 phase- and amplitude-corrected Fourier transformation of the k^3 weighted exafs spectrum

In case of the octahedral coordination of Tc in the $Tc(acac)_3^0$ complex, the symmetric first shell of oxygen atoms would result in one single peak with a symmetrical imaginary part after phase and amplutide corrected Fourier transformation of the EXAFS signal. This symmetrical single peak would have its maximum at the top of the absolute magnitude and at the correct coordination distance.[4] The presence of two maxima in the imaginary part under the nearest neighbor signal in the RDF (Fig. S2) after phase- and amplitude-corrected FT of the k^3 weighted EXAFS spectrum was interpreted as an indication for the presence of a second species

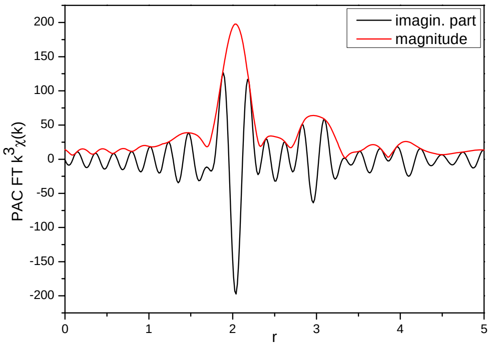

Fig. S2 phase- and amplitude-corrected Fourier transformation of the k^3 weighted exafs spectrum

S3: exafs data and $Tc(acac)_3^0$ signal reconstructed with the parameters in Table 1.

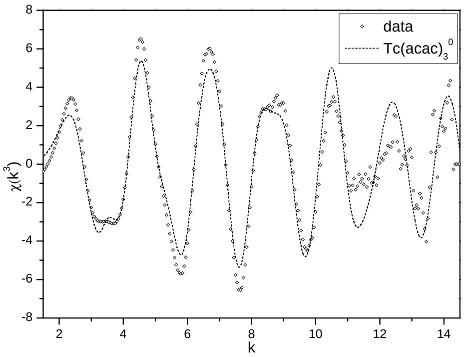

Fig. S3: exafs data and $Tc(acac)_3^0$ signal reconstructed with the parameters in Table 1.

S4 Feff8 input files for the $Tc(acac)_3$ and $TcO(OH)_2(H2O)_3$ compounds, also indicating the DFT optimised geometries for these molecules.

```
TITLE  Tc(acac)3^0
EDGE    K
S02     1
CONTROL 1     1     1     1     1     1
PRINT   5     0     0     1     1     3
EXCHANGE      3     5   0.8     0
AFOLP 1.3
EXAFS   15
RMAX    5
NLEG    6
XANES   12     0.07    2
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```
POTENTIALS
    0    43   Tc
    1     8   O
    2     6   C1
    3     6   C2
    4     6   C3
    5     1   H
    6     1   H

ATOMS
  -0.0052  -0.0001  -0.0000   0    Tc   0.0000
   0.0167  -1.6941   1.1586   1    O    2.0524
   0.0015   1.6942  -1.1585   1    O    2.0525
   1.4505   0.8534   1.1688   1    O    2.0527
   1.4579  -0.8404  -1.1692   1    O    2.0528
  -1.4779   0.8236   1.1701   1    O    2.0524
  -1.4706  -0.8370  -1.1699   1    O    2.0534
   0.7597  -2.7280   1.0103   2    C1   3.0079
   0.7348   2.7349  -1.0102   2    C1   3.0080
   2.0085  -1.9883  -1.0208   2    C1   3.0083
  -2.7391  -0.7318  -1.0200   2    C1   3.0083
  -2.7455   0.7073   1.0202   2    C1   3.0084
   1.9908   2.0062   1.0205   2    C1   3.0084
  -3.3850  -0.0151   0.0001   3    C2   3.3798
   1.7126  -2.9109  -0.0047   3    C2   3.3799
   1.6863   2.9263   0.0047   3    C2   3.3801
   0.5434  -3.8097   2.0452   4    C3   4.3585
   0.5084   3.8147  -2.0449   4    C3   4.3587
   3.0601  -2.3185  -2.0567   4    C3   4.3590
   3.0397   2.3456   2.0561   4    C3   4.3590
  -3.5570  -1.4650  -2.0599   4    C3   4.3594
  -3.5698   1.4332   2.0602   4    C3   4.3595
  -4.4686  -0.0198   0.0000   5    H    4.4634
   2.2654  -3.8429  -0.0040   5    H    4.4635
   2.2306   3.8633   0.0041   5    H    4.4637
  -3.2612  -2.5200  -2.0801   5    H    4.6128
  -3.2840   2.4910   2.0797   5    H    4.6132
   3.8275  -1.5360  -2.0602   5    H    4.6144
   3.8141   1.5702   2.0593   5    H    4.6145
  -0.5482   4.1058  -2.0441   5    H    4.6186
  -0.5105  -4.1104   2.0450   5    H    4.6186
   0.7317   3.4175  -3.0418   5    H    4.6342
   0.7636  -3.4104   3.0421   5    H    4.6342
   2.6025  -2.3245  -3.0527   5    H    4.6392
   2.5824   2.3474   3.0523   5    H    4.6393
  -3.3499   1.0224   3.0525   5    H    4.6422
  -3.3415  -1.0517  -3.0521   5    H    4.6424
   1.1678  -4.6888   1.8673   6    H    5.1814
   1.1249   4.6993  -1.8670   6    H    5.1814
  -4.6311  -1.3958  -1.8709   6    H    5.1814
  -4.6433   1.3538   1.8717   6    H    5.1815
   3.5346  -3.2863  -1.8765   6    H    5.1818
   3.5054   3.3177   1.8759   6    H    5.1818

TITLE   TcO(OH)2(H2O)3
EDGE    K
S02     1
CONTROL 1     1     1     1     1     1
PRINT   5     0     0     1     1     3
EXCHANGE      3     9   0.8     0
AFOLP 1.3
EXAFS   15
RMAX    5
NLEG    4
XANES   12    0.07   2
POTENTIALS
    0    43   Tc
    1     8   O
    2     8   O
    3     8   O
    4     1   H
    5     8   O
ATOMS
   0.0734  -0.1928   0.0147   0    Tc   0.0000
   0.4034  -1.8779  -0.1816   1    O    1.7283
   1.2344   0.4991   1.4425   2    O    1.9660
  -1.3223   0.2468  -1.4091   2    O    2.0417
  -1.8763  -0.7049   0.8919   3    O    2.1984
   2.0277   0.3030  -0.8970   3    O    2.2128
  -2.3479  -0.5446   0.0384   4    H    2.4468
   2.4140   0.5306  -0.0153   4    H    2.4500
  -0.7631   2.1692   0.1818   5    O    2.5113
  -1.2096   1.8878  -0.6533   4    H    2.5340
   0.8171   0.6142   2.3095   4    H    2.5437
  -1.8067  -1.6744   0.9715   4    H    2.5779
   2.3725  -0.5828  -1.1166   4    H    2.5919
  -0.9874   0.2180  -2.3175   4    H    2.5948
  -0.0388   2.7605  -0.0760   4    H    2.9568
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