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

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- Technetium (Tc), radioactive element with rich redox (-1 to +7) and coordination chemistry
- Important for nuclear medicine and high level radioactive waste.
- Tc^{4+} hydrolysis described as (TcX^{2+}, $TcX(OH)^{+}$, $TcX(OH)_2$ and $TcX(OH)^{3-}$, with X either an oxygroup or two hydroxyls)
- $[Tc=O]^{2+}$ postulated, but not confirmed

- EXAFS single scattering (SS) analysis → fairly easy
- Multiple scattering (MS) analysis → detailed geometry required for calculation of phase shifts and amplitudes

$[Tc(acac)_3]^0$ synthesis

- Similar to Abrams et al. (1983). Inorg Chim. Act. 77, L235
- 4.6 ml 2.5M NaOH + 5.5ml EtOH + 2.8 ml acetylacetone + 39 mg $Na_2S_2O_4$ + 200 µl 6.2x10^{-2} M NH_4TcO_4
- 24 hours reaction at 65°C
- Extraction from aq. solution with 4-methyl-2-pentanone (MIBK) in a glovebox (N_2/H_2 95/5%; < 2 ppm O_2)
- Extract concentrated to 2 ml using vacuum distillation at 25°C with liquid nitrogen condensation stage

XAS measurement and analysis

- Transmission mode measurements at ROBL, ESRF

EXAFSPAK

- Data recalibration
- Averaging raw data

ATHENA

- Data reduction

ARTEMIS

- Fitting
  1) SS
  2) MS

- EXAFS data fitting
  - k-space
  - S_0 = 1
  - E0 float, all paths equal
  - N = fixed
  - σ^2 = float
  - R = float

DFT

- g03 rev. D.02
  - UB3LYP
  - LANL2DZ : Tc
  - 6-31G(d) : C, H, O

FEFF

- feff 8.2
  - all atom

Results

Table 1: EXAFS fit data

Path[a]	N	R	σ^2	S_0^2	R-fact[b]
Tc_1-O	6	2.030	0.00136		0.2631
Tc_1-C_1	6	2.964	0.00212		0.2298
Tc_1-C_2	3	3.318	0.00188	$S_0^2(Tc_1)$[e]	0.2187
Tc_1-O-Tc_1-O	6	4.097	0.00271		0.1491
Tc_1-C_1-O	12	3.098	*0.008*[c]		0.0794
Tc_2-O_1	1	1.728			
Tc_2-O_2	2	1.966	σ^2 (Tc_1-O)	$S_0^2(Tc_2)$[e]	0.0317
Tc_2-O_3	2	2.198			
Tc_2-O_4	1	2.511			
Tc_1-C_3	6	4.396	*0.004*[c]		0.0304
Tc_1-C_3-O	12	4.430[d]	0.01292[d]	$S_0^2(Tc_1)$[e]	0.0284
Tc_1-O-C_3-O	6	4.415[d]	0.00892[d]		
Tc_1-C_1-C_3-O	12	4.503[d]	0.01441[d]		
$S_0^2(Tc_1)$	0.6135		$\Delta E_0(Tc_1)$	-1.557	
$S_0^2(Tc_2)$	0. 3865		$\Delta E_0(Tc_2)$	-3.828	

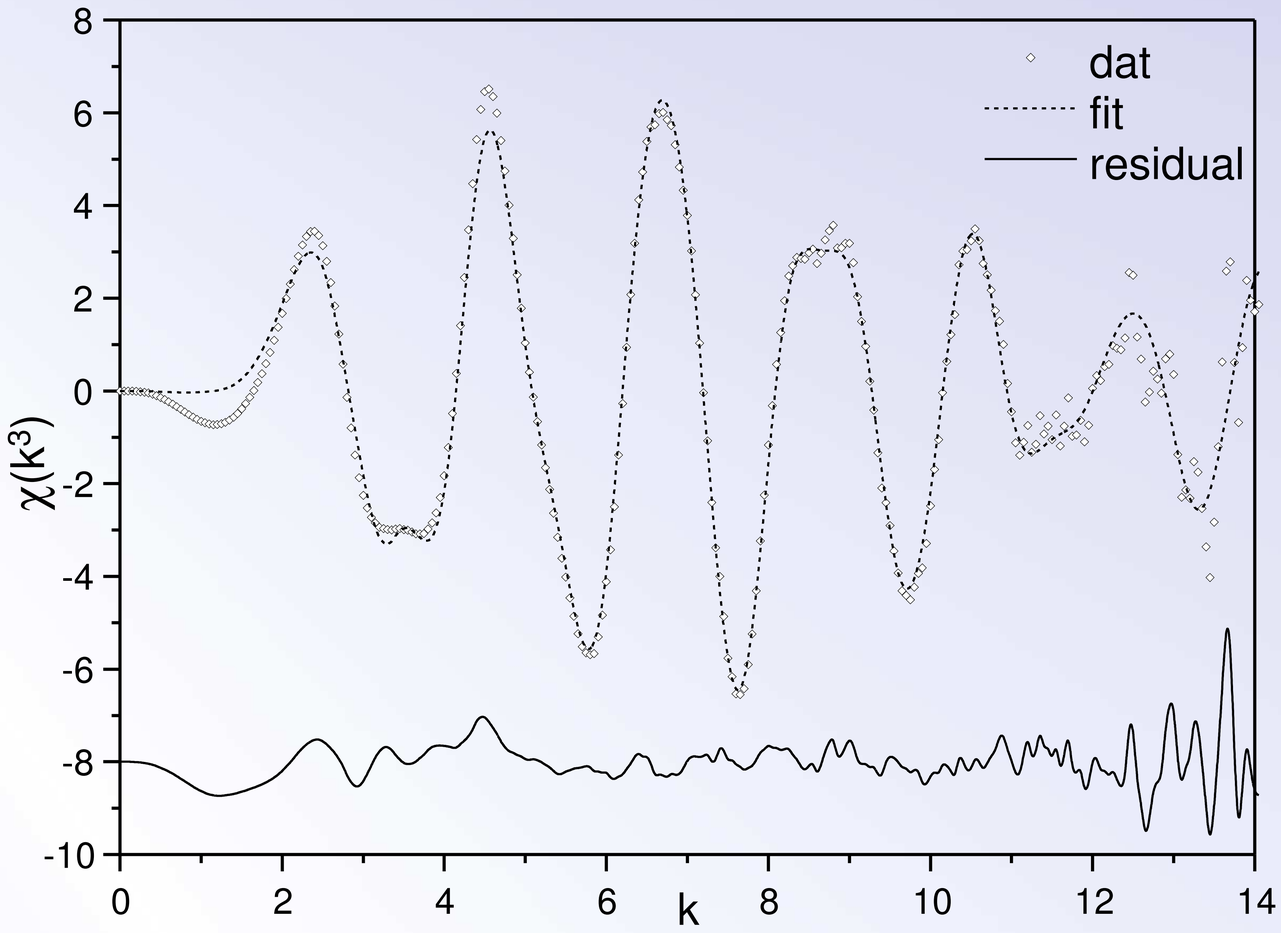
[a] Tc_1: $Tc(acac)_3^0$; Tc_2: $TcO(OH)_2(H_2O)_3$. [b] R factor is shown for each path added to the fit, all other parameter show the final fit values. [c] fixed. [d] evaluated as function of path parameters. [e] $S_0^2(Tc_1) = 1 - S_0^2(Tc_2)$

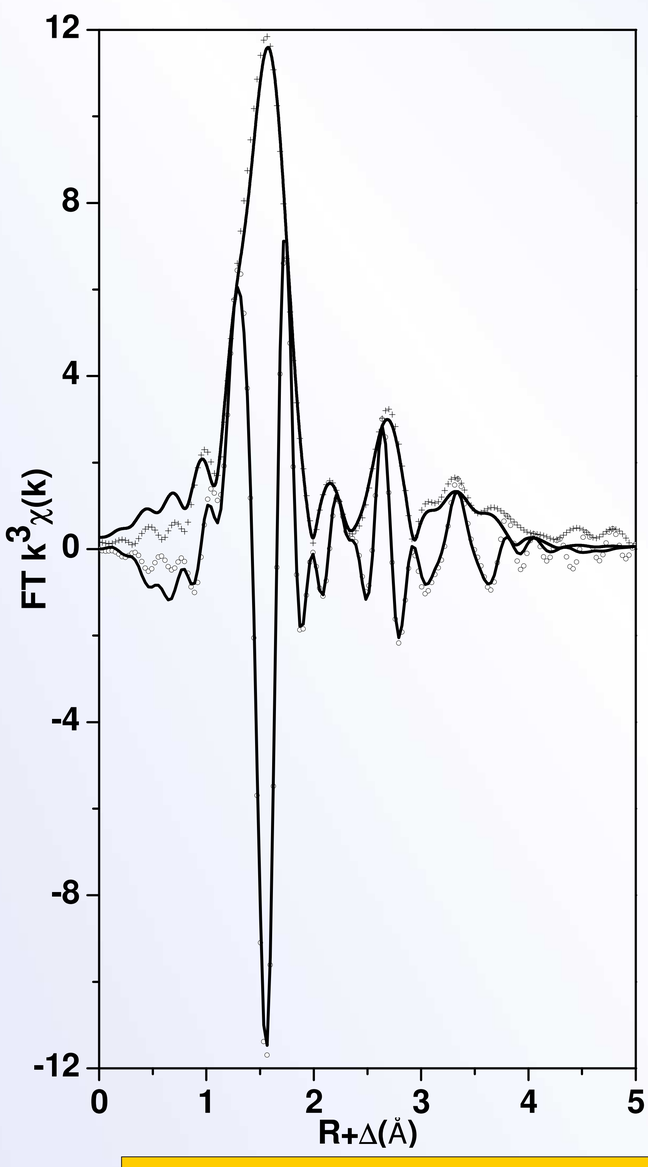
- $TcO(OH)_2(H2O)_x$ detected in $[Tc(acac)_3]^\circ$ reference
- Impurity not visible in UV/Vis spectra
- EXAFS fitted with 30/70% $TcO(OH)_2(H2O)_x$ / $[Tc(acac)_3]^\circ$
- XANES linear combination fit with FEFF8 generated ab inito XANES spectra results in same ratio

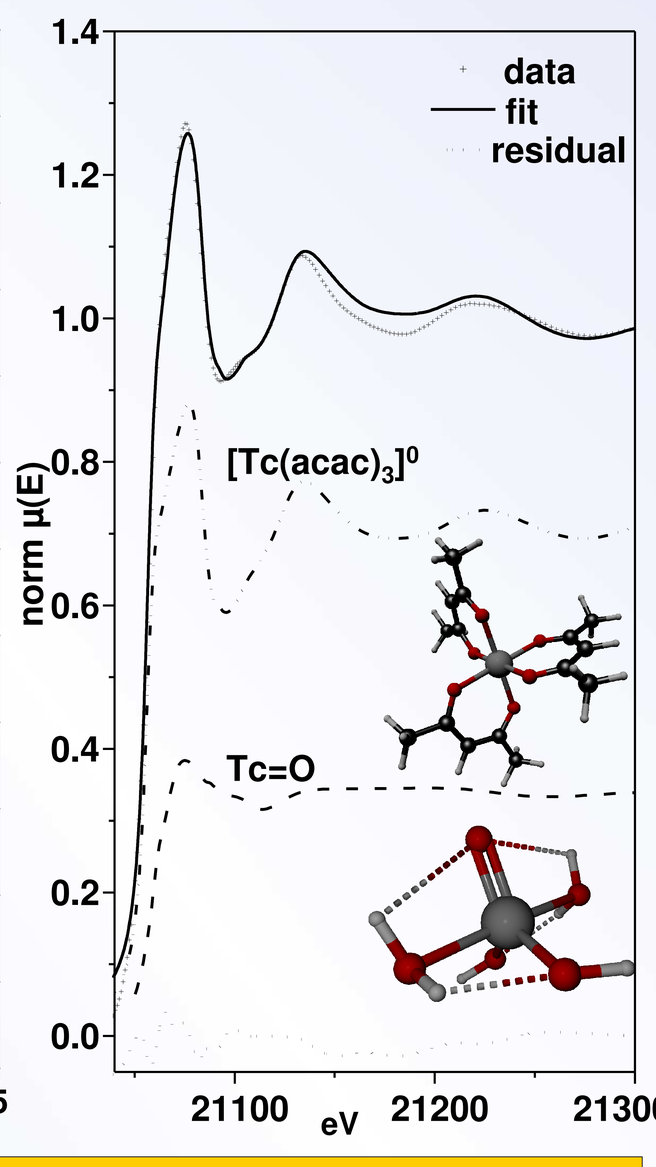
Table 2: Comparison EXAFS fitted distances (Å) with DFT and XRD[a]

Path	EXAFS	DFT	XRD[a]
Tc-O	2.030	2.053	2.025
Tc-C_1	2.964	3.008	2.945
Tc-C_2	3.318	3.380	3.295
Tc-C_3	4.396	4.359	4.296

K. Hashimoto *et al.* Chem. Lett., 1988, 1379-1380.D







Conclusions

- EXAFS + DFT → detailed structure elucidation
- Excellent agreement between EXAFS/DFT derived and single crystal XRD $[Tc(acac)_3]^0$ structure
- Tc^{4+} 'oxy' coordination identified for the first time

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