Supporting Information

Titanium(IV) Citrate Speciation and Structure Under Environmentally and Biologically Relevant Conditions

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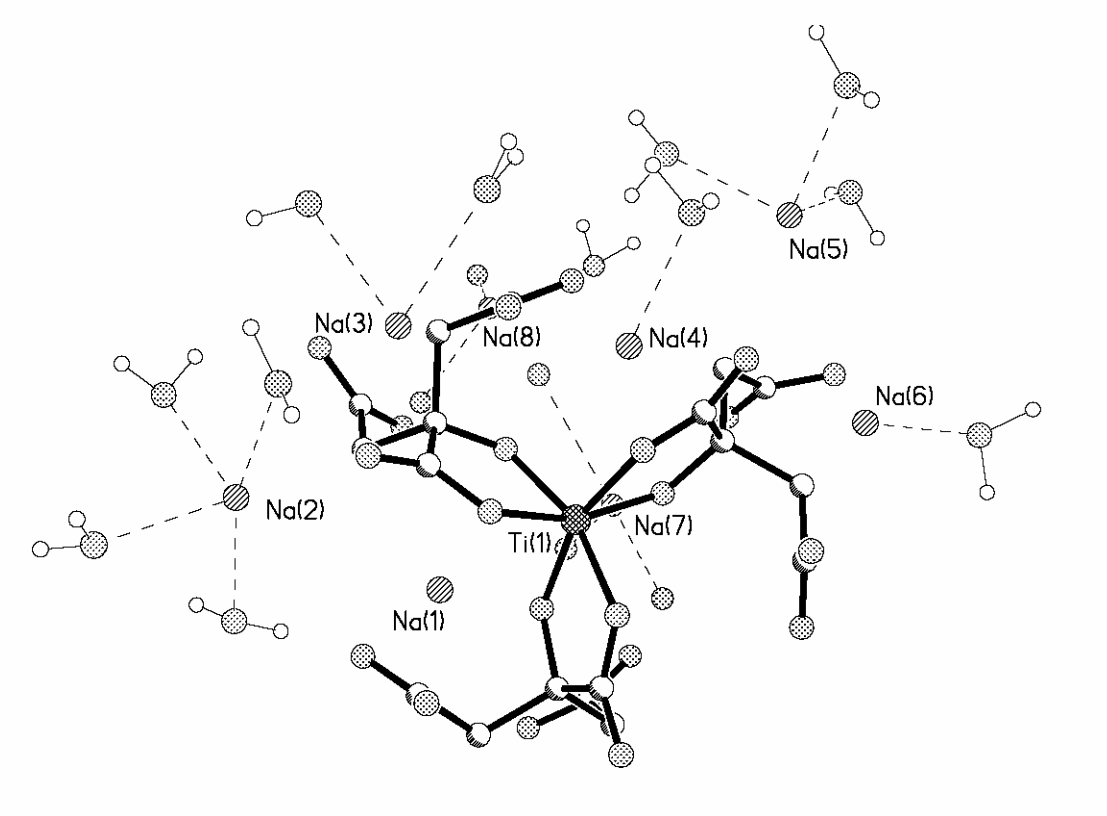
Figure S1. X-ray crystal structure of $Na_8[Ti(C_6H_4O_7)_3]\cdot 17H_2O$ with counterions and lattice waters included.

Figure S2. Potentiometric titration data with overlaid fit from the program BEST (see article for reference) for citrate alone (+) (σ_{fit}=0.003759) and for 3.8:1 citrate:Ti(IV) (●) (σ_{fit}=0.023319). The value on the x-axis, *a*, represents the net moles of base added per mole of ligand.

Table S1. Comparison of goodness-of-fit (σ_{fit}) values for representative least-square fits using the program BEST.



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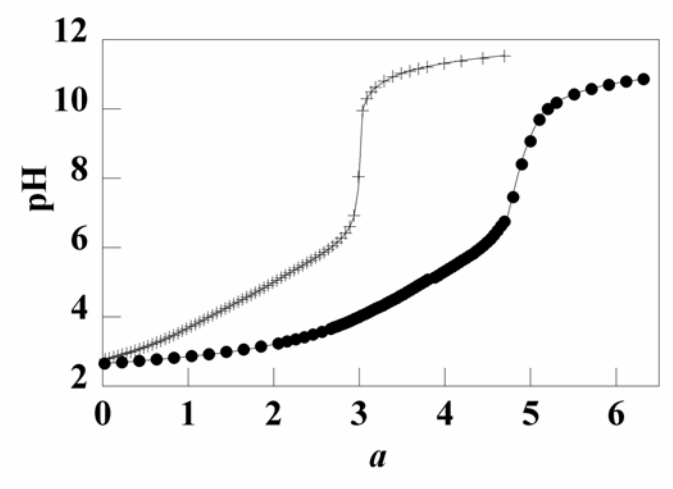

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Table S1. Comparison of goodness-of-fit (σ_{fit}) values for representative least-square fits using the program BEST.

Description[a]	Fitted species (in β_{LMH} notation[b])	σ_{fit}
titration of ligand alone[c]	β_{101}, β_{102}, β_{103}	0.003758
reported speciation[d]	β_{110}, β_{313}, β_{311}, $\beta_{31\text{-}1}$, $\beta_{31\text{-}3}$, $\beta_{21\text{-}4}$	0.023319
unevenly-charged 3:1 complexes	β_{110}, β_{312}, β_{310}, $\beta_{31\text{-}2}$, $\beta_{31\text{-}3}$, $\beta_{21\text{-}4}$	0.028478
all reasonable 3:1 complexes	β_{313}, β_{312}, β_{311}, β_{310}, $\beta_{31\text{-}1}$, $\beta_{31\text{-}2}$, $\beta_{31\text{-}3}$	0.029345
six 2:1 species	β_{212}, β_{211}, β_{210}, $\beta_{21\text{-}1}$, $\beta_{21\text{-}2}$, $\beta_{21\text{-}4}$	0.050255
starting with 20 reasonable species (none hydrolytic)[e]	β_{110}, $\beta_{11\text{-}3}$, β_{313}, β_{310}, $\beta_{31\text{-}3}$, $\beta_{21\text{-}4}$	0.079971
hyodrolytic ($TiOH_n^{4-n}$) species only	$\beta_{01\text{-}1}$, $\beta_{01\text{-}2}$, $\beta_{01\text{-}3}$, $\beta_{01\text{-}4}$, $\beta_{01\text{-}5}$, $\beta_{01\text{-}6}$	>0.15[f]

[a] All of the data in this table were generated from the L:M 3.8:1 titration. The following were held as constants for all fits: cit_{total} = 0.0500 mmol; Ti^{4+}_{total} = 0.0128 mmol; titrateable H^{+}_{total} = 0.200 mmol; xsH = 0.1412 mmol; log β_{101} = 5.6753; log β_{102} = 9.9861; log β_{103} = 12.8700; log $\beta_{00\text{-}1}$ = -13.79.

[b] L = $Hcit^{3-}$; M = Ti^{4+}; H = H^{+}.

[c,d] See overlay of these fits with the respective experimental data in Figure S2.

[e] 6 1:1 species, 7 2:1 species, 7 3:1 species; all but six were ultimately rejected as being insignificant by the fitting algorithm. The inherent problem with this approach is the initial estimates made for the log β values; some bias, if introduced here, can lead to "random" minimizations, where reasonable fits are obtained for unreasonable models.

[f] Depending on the starting values, optimization eliminated all but 2 or 3 of these and they only fit the beginning and end of the experimental pH range.