

Supplementary material

Oxidation of Cr^{III} aminocarboxylate complexes by hydrous manganese oxide: products and time course behaviour

Richard F. Carbonaro^{A,B,D} and Alan T. Stone^C

^ADepartment of Civil and Environmental Engineering, Manhattan College, Riverdale, NY 10471, USA.

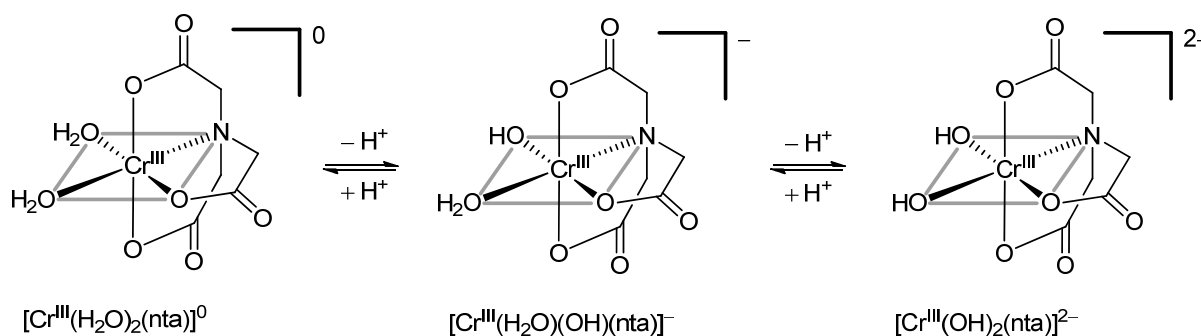
^BMutch Associates, LLC, Ramsey, NJ 07446, USA.

^CDepartment of Geography and Environmental Engineering, G.W.C. Whiting School of Engineering, Johns Hopkins University, Baltimore, MD 21218, USA.

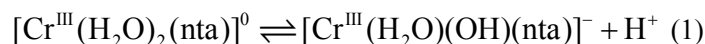
^DCorresponding author. Email: richard.carbonaro@manhattan.edu

Background on speciation of Cr^{III}-NTA and Cr^{III}-IDA

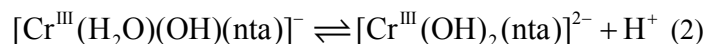
The 1 : 1 Cr^{III} complex with NTA undergoes rapid protonation/deprotonation reactions in aqueous solution^[1-3]:



The predominant form of the 1 : 1 complex between Cr^{III} and NTA in moderately acidic solution is $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{nta})]^0$. Upon raising the pH, one coordinated water molecule deprotonates to form $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{OH})(\text{nta})]^-$ ($\text{p}K_{\text{a}1} = 5.87$; 25 °C, $I = 0.1 \text{ mol L}^{-1}$).^[3]



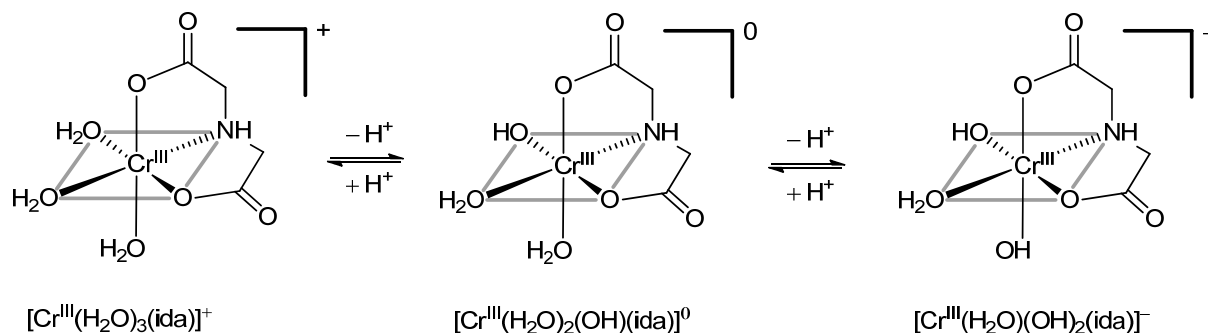
As the pH is increased further, the second aquo ligand deprotonates to form $[\text{Cr}^{\text{III}}(\text{OH})_2(\text{nta})]^{2-}$ ($\text{p}K_{\text{a}2} = 8.74$; 25 °C, $I = 0.1 \text{ mol L}^{-1}$).^[3]



Note that a third $\text{p}K_{\text{a}}$ has been reported at 11.81 (25 °C, $I = 0.1 \text{ mol L}^{-1}$),^[3] but this species is important to the Cr^{III}-NTA mole balance outside the pH range of the experiments with HMO. These protonation/deprotonation reactions are very rapid since Cr^{III} ligand exchange is not involved. However,

dissociation of the Cr^{III} -NTA complex is quite slow as a result of substitution-inert Cr^{III} . Thus, capillary electrophoresis analysis of solutions containing $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{nta})]^0$, $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{OH})(\text{nta})]^-$, and $[\text{Cr}^{\text{III}}(\text{OH})_2(\text{nta})]^{2-}$ yield a single sharp peak,^[4] which we refer to as ‘ Cr^{III} -NTA.’

Similar reactions exist for the 1 : 1 complex between Cr^{III} and IDA^[5]:



The predominant form of the 1 : 1 complex of Cr^{III} and IDA in moderately acidic solution is $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_3(\text{ida})]^+$. As the pH of solutions containing $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_3(\text{ida})]^+$ is increased, one coordinated water molecule deprotonates to form $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{OH})(\text{ida})]^0$. Increasing the pH further results in deprotonation of a second coordinated water molecule to form $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{OH})_2(\text{ida})]^-$. The exact values for $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ for these reactions are not known. On the basis of electrophoretic measurements, $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ were respectively estimated to be ~ 6 and 8 .^[4] CE analysis of solutions containing $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_3(\text{ida})]^+$, $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2(\text{OH})(\text{ida})]^0$ and $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{OH})_2(\text{ida})]^-$ yield one sharp peak,^[4] which we refer to as ‘ Cr^{III} -IDA’.

Supplementary Cr^{III} alum oxidation results

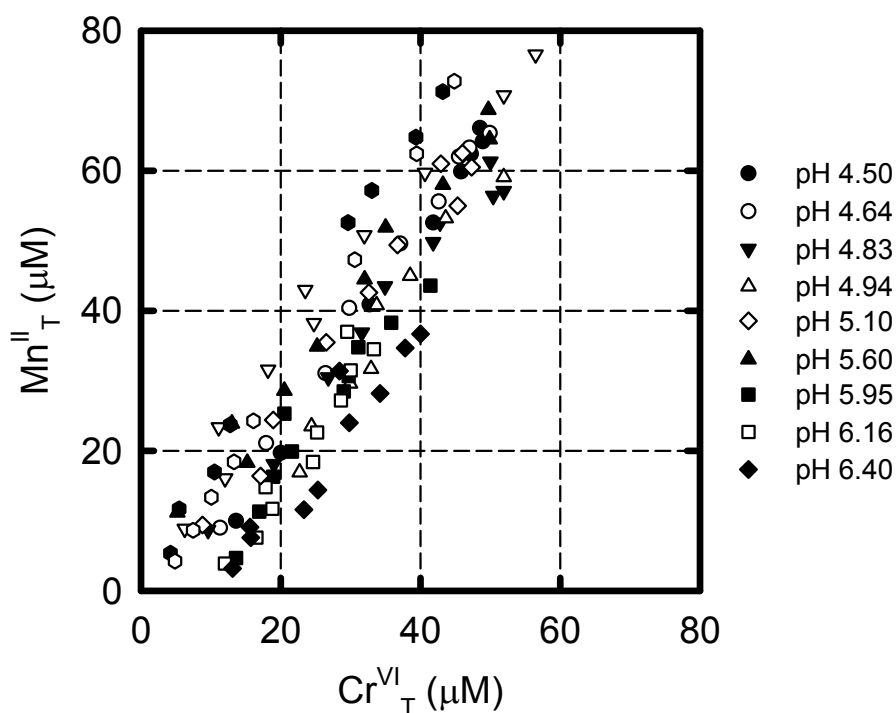


Fig. S1. $\text{Mn}^{\text{II}}_{\text{T}}$ v. $\text{Cr}^{\text{VI}}_{\text{T}}$ for all Cr^{III} alum oxidation experiments performed at an HMO loading of 0.5 mM. All experiments employed 10 mM acetate or MES buffer and 10 mM NaCl.

Table S1. Rate constants for Cr^{VI}_T production in suspensions containing 50 μM Cr^{III} alum and HMO

Cr^{III} alum stock solutions were prepared from $\text{KCr}^{\text{III}}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(\text{s})$. Loading ($[\text{HMO}]_0$) expressed as moles of added manganese per litre of suspension. Surface area loading (HMO_0) calculated using the nitrogen Brunauer, Emmett and Teller (BET) surface area determination. k_{obs} calculated using Eqn 10 (see text). k'_{obs} is k_{obs} divided by the surface area loading

pH	$[\text{HMO}]_0$ (mM)	HMO_0 ($\text{m}^2 \text{L}^{-1}$)	k_{obs} (min^{-1})	k'_{obs} ($\text{L m}^{-2} \text{s}^{-1}$)	$\text{Cr}^{\text{VI}}_{\text{T,max}}$ (μM)
4.50	0.50	13	0.69	8.8×10^{-4}	49.4
4.64	0.50	13	0.56	7.1×10^{-4}	49.9
4.83	0.50	13	0.57	7.3×10^{-4}	51.9
4.94	0.50	13	0.65	8.3×10^{-4}	51.9
5.10	0.50	13	0.48	6.1×10^{-4}	47.3
5.60	0.50	13	0.33	4.2×10^{-4}	49.9
5.95	0.50	13	–	–	41.4
6.16	0.50	13	–	–	33.3
6.40	0.50	13	–	–	40.0
6.62	0.50	13	–	–	37.0

Table S2. Summary of all Cr^{III}-IDA and Cr^{III}-NTA oxidation experiments

	HMO (mM)	Buffer	pH	Added at start of experiment	Figure(s)
[Cr^{III}-NTA]₀ (μM)					
54	0.5	10 mM HAc	4.66	–	5a, 14a
54	1.0	10 mM HAc	4.66	–	5b, 14a
54	5.0	10 mM HAc	4.71	–	5c, 14b
54	5.0	10 mM HAc	4.76	–	6a, 6b
54	5.0	10 mM HAc	5.23	–	6a, 6b, 7a, 14b
54	5.0	10 mM MES	6.16	–	6a, 6b
54	5.0	10 mM MES	6.53	–	6a, 6b, 7b
54	5.0	10 mM MOPS	7.00	–	6a, 6b, 8a–d
54	5.0	10 mM MOPS	7.25	–	6a, 6b, 7c, 9a–c
54	5.0	10 mM EPPS	7.77	–	6a, 6b
54	5.0	10 mM CHES	8.48	–	6a, 6b
54	5.0	10 mM CHES	9.31	–	6a, 6b, 7d
54	5.0	10 mM HAc	4.46	–	14b
54	5.0	10 mM MOPS	7.06	50 μM MnCl ₂	15a–d
54	5.0	10 mM MOPS	7.05	100 μM MnCl ₂	15a–d, S2
54	5.0	10 mM MOPS	7.04	200 μM MnCl ₂	15a–d
54	5.0	10 mM MOPS	7.06	100 μM ZnCl ₂	S3a–b
[Cr^{III}-IDA]₀ (μM)					
50	0.15	10 mM HAc	4.67	–	11a
50	0.30	10 mM HAc	4.69	–	13a
50	0.5	10 mM HAc	4.65	–	11b, 13d
50	1.0	10 mM HAc	4.65	–	11c, 12b, 13e, 16a–d, S2a–f
50	5.0	10 mM HAc	4.73	–	11d
50	5.0	10 mM HAc	4.17	–	Not shown
50	1.0	10 mM HAc	4.32	–	12a
50	1.0	10 mM HAc	5.17	–	12c, 13f
50	1.0	10 mM MES	5.77	–	12d
50	1.0	10 mM MES	6.23	–	Not shown
50	1.0	10 mM HAc	4.67	50 μM MnCl ₂	16a–d
50	1.0	10 mM HAc	4.69	100 μM MnCl ₂	16a–d
50	1.0	10 mM HAc	4.70	50 μM ZnCl ₂	S2a–f
50	1.0	10 mM HAc	4.70	100 μM ZnCl ₂	S2a–f

Supplementary Cr^{III}-NTA and Cr^{III}-IDA oxidation results

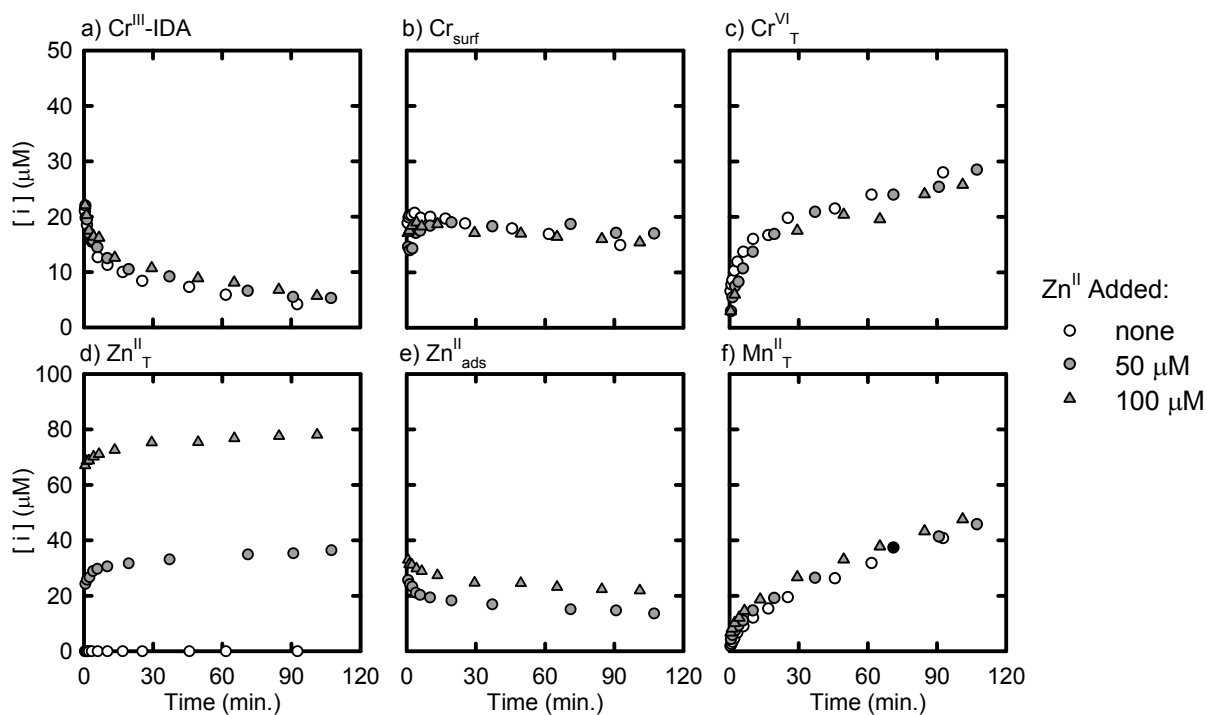


Fig. S2. Reaction of 50 μM Cr^{III}-IDA with 1.0 mM HMO at pH 4.7 where no divalent metal ion was added, and where 50 and 100 μM Zn^{II} was added before initiation of the reaction. Experiments employed 10 mM acetate to buffer pH and 10 mM NaCl.

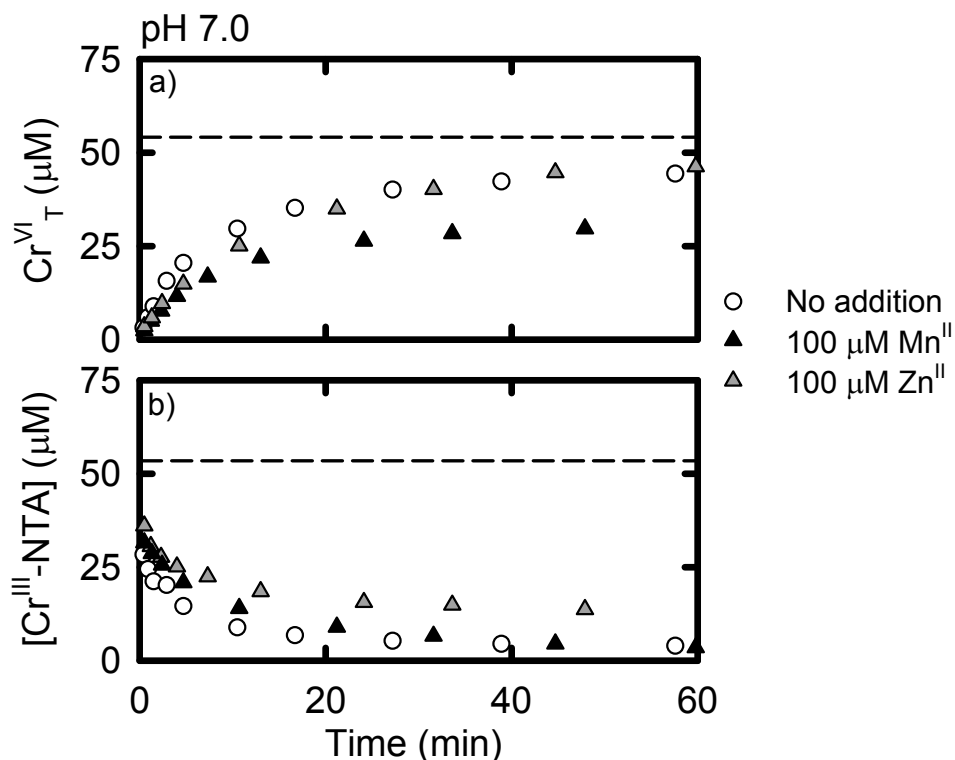


Fig. S3. Reaction of 54 μM $\text{Cr}^{\text{III}}\text{-NTA}$ with 5.0 mM HMO at pH 7.0 where no divalent metal ion was added, and where 100 μM Zn^{II} and 100 μM Mn^{II} were added before initiation of the reaction. All experiments employed 10 mM MOPS buffer and 10 mM NaCl.

References

- [1] H. Visser, W. Purcell, S. Basson, Q. Claassen, The synthesis and crystal structures of $\text{Cs}_2[\text{Co}_2(\text{nta})_2(\text{m-OH})_2] \cdot 4\text{H}_2\text{O}$ and $(\text{C}_{10}\text{H}_{10}\text{N}_3)_2[\text{CoCl}_4]$. *Polyhedron* **1997**, *16*, 2851. doi:10.1016/S0277-5387(97)00012-0
- [2] H. G. Visser, J. G. Leipoldy, W. Purcell, Substitution and protonation reactions of nitrilotriacetatochromium(III) ions. *Polyhedron* **1994**, *13*, 1051. doi:10.1016/S0277-5387(00)83031-4
- [3] H. M. N. H. Irving, R. H. Al-Jarrah, Complexes of chromium(III) with nitrilotriacetic acid and their extraction by solutions of aliquat-336 in dichloroethane. *Anal. Chim. Acta* **1972**, *60*, 345. doi:10.1016/S0003-2670(01)95011-1
- [4] R. F. Carbonaro, A. T. Stone, Speciation of chromium(III) and cobalt(III) (amino)carboxylate complexes using capillary electrophoresis. *Anal. Chem.* **2005**, *77*, 155. doi:10.1021/ac048860b
- [5] J. A. Weyh, R. E. Hamm, Iminodiacetato, methyliminodiacetato and 1,3-propanediaminetetraacetato complexes of chromium(III). *Inorg. Chem.* **1968**, *7*, 2431. doi:10.1021/ic50069a049