

Complexation of Np(V) with the dicarboxylates malonate and succinate: complex stoichiometry, thermodynamic data and structural information – Supplementary information

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Supporting Information

Tables

Table S1: Thermodynamic stability constants $\log \beta_n^0(\Theta)$ for the formation of $[NpO_2(Mal)]^{1-2n}$ ($n = 1, 2$) obtained from $NaClO_4$ and $NaCl$ media and their mean values as a function of temperature.

Θ [°C]	20	30	40	50	60	70	80	85	
$NpO_2(Mal)^-$	NaClO ₄	3.31	3.38	3.38	3.48	3.48	3.52	3.54	3.61
		0.06	0.06	0.08	0.08	0.06	0.10	0.06	0.08
	NaCl	3.32	3.43	3.45	3.53	3.53	3.56	3.58	3.61
		0.06	0.07	0.08	0.08	0.08	0.08	0.09	0.07

	\emptyset	3.31	3.41	3.42	3.51	3.50	3.54	3.56	3.61
		0.07	0.08	0.09	0.08	0.09	0.08	0.09	0.08
	NaClO ₄	3.90	4.00	4.03	4.15	4.18	4.23	4.27	4.33
		0.06	0.08	0.08	0.06	0.06	0.10	0.08	0.12
	NaCl	3.91	3.98	4.06	4.15	4.21	4.27	4.32	4.37
		0.11	0.07	0.10	0.09	0.14	0.10	0.10	0.10
	\emptyset	3.90	3.99	4.04	4.20	4.20	4.25	4.30	4.35
		0.11	0.08	0.10	0.09	0.14	0.11	0.11	0.12

Table S2 Thermodynamic stability constants $\log \beta_{\text{0}}^{\text{0}}(\Theta)$ for the formation of $[\text{NpO}_2(\text{Succ})_n]^{1-2n}$ ($n = 1, 2$) obtained from NaClO₄ and NaCl media and their mean values as a function of temperature.

	Θ [°C]	20	30	40	50	60	70	80	85
	NaClO ₄	2.13	2.00	1.99	2.11	2.15	2.23	2.44	2.49
		0.12	0.09	0.07	0.06	0.06	0.09	0.17	0.12
	NaCl	2.13	2.23	2.26	2.28	2.38	2.49	2.62	2.64
		0.10	0.10	0.08	0.08	0.11	0.06	0.11	0.18
	\emptyset	2.13	2.11	2.12	2.19	2.26	2.36	2.53	2.56
		0.15	0.14	0.10	0.10	0.12	0.11	0.20	0.22
	NaClO ₄				1.32	1.51	1.61	1.80	2.13
		-	-	-	0.19	0.07	0.12	0.19	0.15
	NaCl				1.49	1.83	1.94	2.19	2.40
		-	-	-	0.10	0.14	0.11	0.11	0.19
	\emptyset				1.41	1.67	1.77	2.00	2.26
		-	-	-	0.21	0.15	0.16	0.22	0.24

Table S3: Fit parameters of the raw k^2 -weighted Np-L₃-edge EXAFS spectra of Np(V) in the presence of malonate as a function of pH_c.

pH _c	7.8	5.2	5.0	4.7	4.4	3.8	3.1
O _{ax}	N	2*	2*	2*	2*	2*	2*
	R / Å	1.83(1)	1.83(1)	1.85(1)	1.83(1)	1.84(1)	1.84(1)
	σ^2 / Å ²	0.0002(3)	0.0009(3)	0.0006(4)	0.0006(3)	0.0004(2)	0.0001(3)
O _{mul}	N	4*	4*	4*	4*	4*	4*
	R / Å	3.67**	3.66**	3.70**	3.66**	3.68**	3.67**
	σ^2 / Å ²	0.0004**	0.0019**	0.0013**	0.0012**	0.0009**	0.0001**
O _{eq}	N	3.9(1.0)	3.7(1.0)	4.0(1.0)	3.5(1.0)	3.8(1.0)	4.0(1.0)
	R / Å	2.46(1)	2.45(1)	2.47(1)	2.46(1)	2.46(1)	2.47(1)
	σ^2 / Å ²	0.0062(14)	0.0046(11)	0.0070(20)	0.0042(13)	0.0066(12)	0.0062(15)
C _c	N	2.7(1.0)	3.7(1.0)	1.9(1.0)	3.0(1.0)	2.0(1.0)	2.5(1.0)
	R / Å	3.39(3)	3.42(2)	3.48(5)	3.41(3)	3.38(5)	3.41(2)
	σ^2 / Å ²	0.004*	0.004*	0.004*	0.004*	0.004*	0.004*
ΔE _o / eV	1.9(5)	2.9(5)	2.7(7)	3.3(5)	2.2(4)	2.9(5)	2.3(4)
Red. error	0.014376	0.0157143	0.024140	0.0189825	0.0100117	0.0179982	0.00741869

* Parameter fixed; ** parameter depending on X(O_{ax}): X(O_{mul}) = 2 · X(O_{ax}). O_{ax} = axial O-atoms, O_{mul} = multi scattering path of axial O-atoms (Np-O-O), O_{eq} = equatorial O-atoms, C_c = C-atoms of coordinating COO⁻ groups.

Table S4: Fit parameters of the raw k^2 -weighted Np-L₃-edge EXAFS spectra of Np(V) in the presence of succinate as a function of pH_c.

pH _c	7.8	6.1	5.2	4.0	0.8
O _{ax}	N	2*	2*	2*	2*
	R / Å	1.84 (1)	1.84 (1)	1.84 (1)	1.84 (1)
	σ^2 / Å ²	0.0005 (4)	0.0001 (4)	0.0003 (4)	0.0014 (4)
O _{mul}	N	4*	4*	4*	4*
	R / Å	3.46 (3)	3.46 (3)	3.50 (3)	3.58 (3)
	σ^2 / Å ²	0.00100	0.0002	0.0005	0.0030
O _{eq}	N	4.7 (1.0)	4.6 (1.0)	5.1 (1.0)	5.1 (1.0)
	R / Å	2.49 (1)	2.48 (1)	2.49 (1)	2.50 (1)
	σ^2 / Å ²	0.0062 (18)	0.0052 (17)	0.0065 (9)	0.0047 (15)
C _c	N	1.1 (1.0)	1.0 (1.0)	0.8 (1.0)	0.5 (1.0)
	R / Å	2.88 (4)	2.78 (5)	2.84 (6)	2.81 (1)
	σ^2 / Å ²	0.003*	0.003*	0.003*	0.003*
ΔE _o / eV	7.9 (6)	7.5 (5)	8.0 (6)	8.6 (5)	7.2 (6)
Red. error	0.0164131	0.0185585	0.0242427	0.0221710	0.0201802

* Parameter fixed; ** parameter depending on X(O_{ax}): X(O_{mul}) = 2 · X(O_{ax}). O_{ax} = axial O-atoms, O_{mul} = multi scattering path of axial O-atoms (Np-O-O), O_{eq} = equatorial O-atoms, C_c = C-atoms of coordinating COO⁻ groups.

Figures

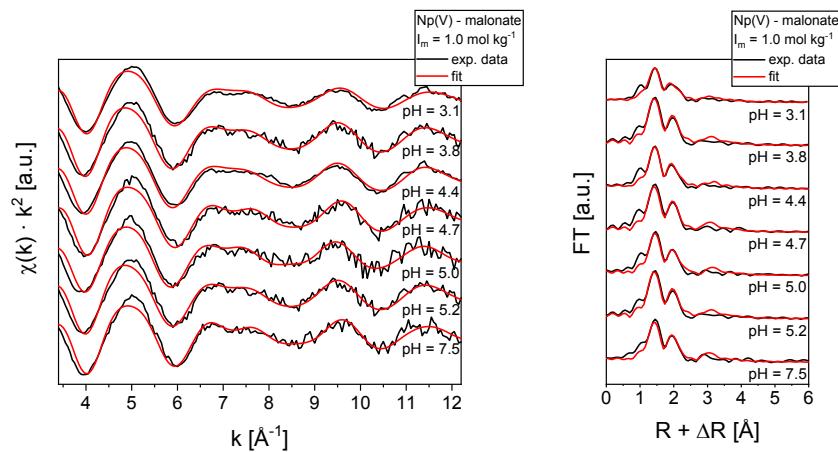


Figure S1: EXAFS analyses of Np(V) in the presence of malonate as a function of the conditional pH_c value. (left) raw k^2 -weighted Np-L₃-edge EXAFS spectra; (right) related Fourier transforms; (black) experimental data; (red) best fit from EXAFSPAK.

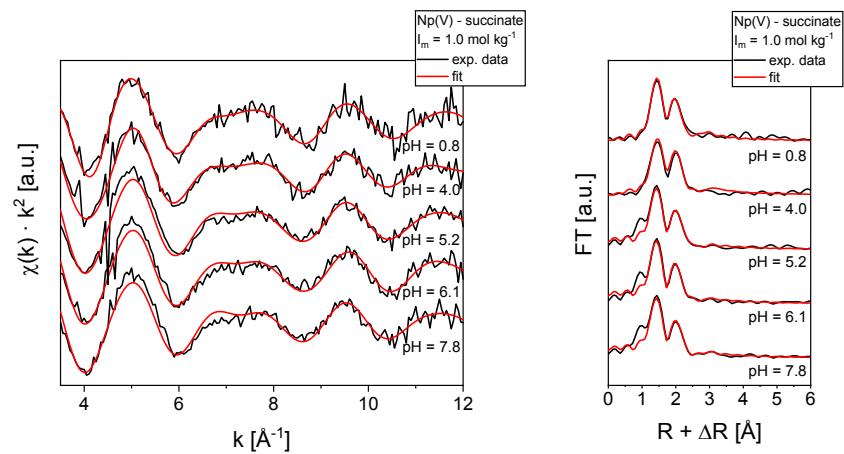


Figure S2: EXAFS analyses of Np(V) in the presence of succinate as a function of the conditional pH_c value. (left) raw k^2 -weighted Np-L₃-edge EXAFS spectra; (right) related Fourier transforms; (black) experimental data; (red) best fit from EXAFSPAK.