Spectrophotometric Studies of Complexes of NpO_2^+ in Solution.
I. Complexes with the Anions of Oxalic, Malonic, Succinic and Maleic Acid*

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The formation constants as well as the spectra of the complexes formed by the neptunyl ion, NpO_2^+, with the anions of oxalic, malonic, succinic and maleic acid have been measured at 1 M ionic strength by full deconvolution of high resolution near-infrared spectra acquired on a specially built high performance spectrophotometer.

The 980.4 nm NpO_2^+ (aq) band is displaced to longer wavelengths on complexation. Program TAFIT, using the Simplex algorithm [1], was used to deconvolute the spectra and compute the best set of stability constants for complex formation. A model giving formation of two complexes of 1:1 and 1:2 stoichiometry was sufficient to give a good fit of the experimental data. Figure 1a gives a typical set of experimental absorption spectra of samples containing a constant concentration of Np(V) and logarithmically increasing amounts of ligand (malonate). Two isosbestic points are evident in this case, corresponding to the equilibria $M + L \rightleftharpoons ML$ and $ML + L \rightleftharpoons ML_2$, respectively. Program TAFIT gave the spectra of the pure species: M, ML and ML_2, as shown in Fig. 1b.

A clear decrease in the complexation stability constant for both the 1:1 and 1:2 complexes is evident along the series oxalate > malonate > succinate (Table I), reflecting the higher stability of five-membered rings. Maleate is a stronger ligand than succinate, since upon complex formation less conformational entropy is lost.

The width (FWHM) of the absorption band in the complexes is always larger than that of pure Np(V) (aq) ions (Table II), because of decreased symmetry in the charge distribution around the central metal ion. Bathochromic displacement (an enthalpic effect) is positively correlated with the stability constants.

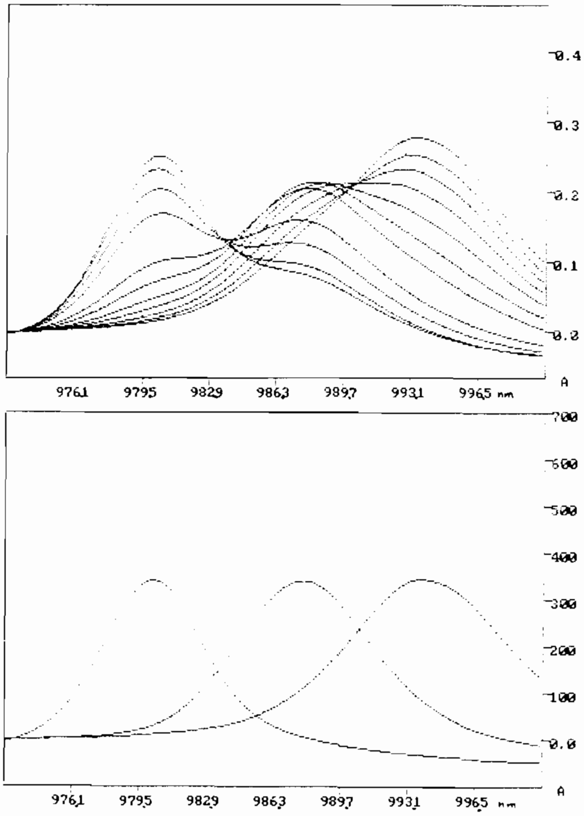

Fig. 1. (a) Typical set of spectra of NpO_2^+–malonate mixtures. NpO_2^+ concentration is 0.944×10^{-3} M. Malonate concentration is 1.2, 1.6, 2.4, 5.2, 8.0, 12.0, 19.2, 28.0, 43.2, 66.0 and 100.0×10^{-3} M. pH = 6.0. Ionic strength is adjusted to 1.0 M with $NaClO_4$. To compensate for baseline fluctuation, all spectra have been normalized to O.D. = 0 at $\lambda = 974$ nm. (b) Deconvolution of the above set of spectra into three components.

TABLE I. Apparent Stability Constants for NpO_2^+ Complexation[a]

Ligand	$\log \beta_{101}$ (app) ($l\ mol^{-2}$)	$\log \beta_{102}$ (app) ($l^2\ mol^{-2}$)
Oxalate	3.52 ± 0.06	6.09 ± 0.06
Malonate	2.48 ± 0.04	4.10 ± 0.02
Succinate	1.45 ± 0.05	2.30 ± 0.15
Maleate	1.74 ± 0.03	2.82 ± 0.08

[a] $\mu = 1.0$ M ($NaClO_4$); $T = 23 \pm 2$ °C, pH = 6.0. In the calculation of the apparent stability constants the residual partial protonation of the ligands has been neglected.

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TABLE II. Shifts and Linewidths of the Absorption Bands of NpO_2^+ Complexes

Ligand	$\Delta\lambda_1$ (nm)	$\Delta\lambda_2$ (nm)	$FWHM_1$ (nm)	$FWHM_2$ (nm)
Oxalate	7.7 ± 0.1	15.4 ± 0.1	7.7 ± 0.1	9.4 ± 0.2
Malonate	7.7 ± 0.1	13.6 ± 0.1	7.9 ± 0.1	9.5 ± 0.1
Succinate	4.5 ± 0.1	8.0 ± 0.5	8.5 ± 0.2	11.5 ± 0.5
Maleate	5.7 ± 0.1	8.4 ± 0.2	8.0 ± 0.1	11.0 ± 0.5

TABLE III. Stability Constants of NpO_2^+ Complexes[a]

Ligand	log β_{101} (=pK_1) (l mol^{-1})	log β_{102} (=pK_1 + pK_2) (l^2 mol^{-2})	Reference	Method	Ionic strength (M)
Oxalate	3.52 ± 0.06	6.09 ± 0.06	p.w.	sp	1
	2.71	4.91	2	sp	0.5
	4.39	7.36	3	i.ex.	0.05
	3.42	5.66	4	s.ex.	→0
	3.74 ± 0.05	6.31 ± 0.10	5	pH	1
Malonate	2.53 ± 0.04	4.20 ± 0.02	p.w.	sp	1
	2.26	3.26	4	s.ex.	→0
	2.75 ± 0.02	–	5	pH	1
Succinate	1.51 ± 0.05	2.42 ± 0.15	p.w.	sp	1
	1.29	1.89	4	s.ex.	→0
	1.72 ± 0.03	–	5	pH	1
Maleate	1.89 ± 0.03	3.12 ± 0.08	p.w.	sp	1
	2.20 ± 0.02	–	5	pH	1

[a] p.w. = present work: 1.0 M ($NaClO_4$) medium, $T = 23 \pm 2$ °C; sp = spectroscopy; s.ex. = solvent extraction. i.ex. = ion exchange; pH = potentiometric titration. Data from Table I were corrected for hydrogen ion complexation at pH 6.0 using the following values for ligand first protonation constant (pK_{a2}): oxalate = 3.60; malonate = 5.11; succinate = 5.20; maleate = 5.62 (from ref. 6).

The computed stability constants, corrected for hydrogen ion complexation, are in good agreement (for 1:1 complex formation data) with results obtained with potentiometric titration experiments (Table III).

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