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Complexation of NpO_2^+ by aromatic polycarboxylates

G.R. Choppin[a,]*, B.E. Stout[b], M. Pagès[b]

[a]*Department of Chemistry, Florida State University, Tallahassee, FL 32306-4390, USA*
[b]*Institut Curie, Section de Physique et Chimie, F-75231 Paris Cedex 05, France*

Abstract

The complexation of Np(V) with aromatic polycarboxylic acids was studied by spectrophotometry at 1 M ionic strength ($NaClO_4$) and 23°C. The stability constants of the 1:1 complexes decreased in the order hemimellitate>mellitate>pyromellitate>trimellitate≈phthalate). After correction for statistical effects, the stability constants with all ligands except hemimellitate were approximately the same. For all systems, the data corresponded to bidentate chelation by the ligand. The greater strength of hemimellitate complexation was attributed to an increase in electron density at the binding site through induction from the non-chelating carboxylate group.

Keywords: Np(V) ; Aromatic polycarboxylic acids; Spectrophotometry; Stability constants; Hemimellitate complexation

1. Introduction

The linear dioxo cations formed by the pentavalent actinides form relatively weak complexes, reflecting an effective charge of ca. +2.3 on the actinide atom [1]. NpO_2^+ is of interest as it forms 'cation–cation' complexes with oxocations such as UO_2^{2+}, VO_2^+ and NpO_2^+, while PuO_2^+ is the predominant form of soluble plutonium found in oxic natural waters. Since hydrolysis and interaction with anions present in natural aquatic systems are relatively weak for NpO_2^+ and PuO_2^+, these species can be rather mobile in such media.

NpO_2^+ has been shown to be present as dimers, $[NpO_2]_2^{2+}$, in solid crystals of $(NpO_2)_3$mellitate·$2H_2O$ [2] and as linear polymeric chains in solid (NpO_2)4 pyromellitate [3] (mellitate = benzenehexacarboxylate, pyromellitate = benzene-1,2,4,5-tetracarboxylate). This has been attributed to the tendency to form the more positive cation–cation complexes to neutralize the high charge density of the Me^{6-} and $Pyrome^{4-}$ anions. In this research we have studied the complexation of NpO_2^+ with these benzene polycarboxylates as well as with phthalate, trimellitate (1,2,4-benzene tricarboxylate) and hemimellitate (1,2,3-benzenetricarboxylate) to ascertain if formation of NpO_2^+ dimers or polymers is present. We were also interested in studying the effect of statistical factors in complexation with these poly-donor systems and whether inductive and/or resonance effects could be observed.

2. Experimental

Stock solutions of 0.1 M NpO_2^+ in dilute $HClO_4$ were prepared by dissolution of a measured amount of solid NpO_2 in concentrated perchloric acid followed by evaporation (three times) to dryness and dissolution of the residue in water. Np(V) was generated by coulometry using a potential of 0.9 V NHE and a platinum electrode in 0.2 M $HClO_4$ [4]. Quantitative conversion to NpO_2^+ was confirmed by measurement of its 980.4-nm absorption band with a Cary 14 spectrophotometer. Distilled, deionized, micro-filtered water (>18 MΩ) was used in all experiments.

The organic ligands (Aldrich Chemical Co.) were used without further purification. Their purity was checked by titration with NaOH solution and found to be 98–100% of theoretical. Stock solutions of the ligands were adjusted to pH 6 with CO_2-free NaOH. The final ionic strength was adjusted to 1.0 M with $NaClO_4$ (Merck). The solutions were buffered at pcH 7.0 and 7.5 with Hepes and at pcH 6.0 and 6.5 with MES. The pH values were measured with an Orion 701 pH combination glass electrode calibrated for pcH ($=-\log[H^+]$ concentration) with a series of solutions

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*Corresponding author. Fax: +1 904 6448281; e-mail: choppin@chemmail.chem.fsu.edu

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Table 1
Protonation constants of aromatic polycarboxylates

Ligand	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6
Mellitate	5.38±0.03	4.43±0.03	3.41±0.03	2.43±0.02	2.08±0.07	1.1±0.2
Pyromellitate	4.85±0.03	3.92±0.02	2.68±0.03	1.8±0.3		
Hemimellitate	5.04±0.01	3.78±0.03	2.63±0.05			
Trimellitate	4.61±0.01	3.58±0.01	2.38±0.01			
Phthalate	4.73±0.01	2.55±0.02				

T=25°C; I=1.0 M ($NaClO_4$).

of 0.01–0.10 M $HClO_4$ adjusted to a total 1.0 M ($NaClO_4$) ionic strength, e.g. for a meter reading of pH=6.00, the pcH=6.14.

The effect of complexation on the 980.4-nm band of NpO_2^+ was measured with a high resolution diode array spectrophotometer built from commercially available components at the Curie Laboratory [5]. The calibrations, resolution, mode of data acquisition, etc., are described in Ref. [5].

The acid dissociation constants were measured by Dr J.-F. Chen by the titration and data analysis methods described in Ref. [6]. The values are listed in Table 1.

3. Results

The absorbance at 980.4 nm of uncomplexed NpO_2^+ over a range of concentrations obeyed the Beer–Lambert law. For each ligand, measurements were made of the absorbance spectra of solutions with a constant total concentration of NpO_2^+ (0.001 M) and 12 concentrations of ligand ranging from 0.0012 to 0.1 M, with at least two runs made of each ligand system at each concentration. The presence of a single, well-defined isosbestic point was seen in all spectra. Typical deconvoluted spectra of the NpO_2^+–mellitate system at pcH 5.0 and 7.5 are shown in Fig. 1. Examples of the parameters of the resolved spectral peaks for NpO_2^+ in the various systems are listed in Table 2.

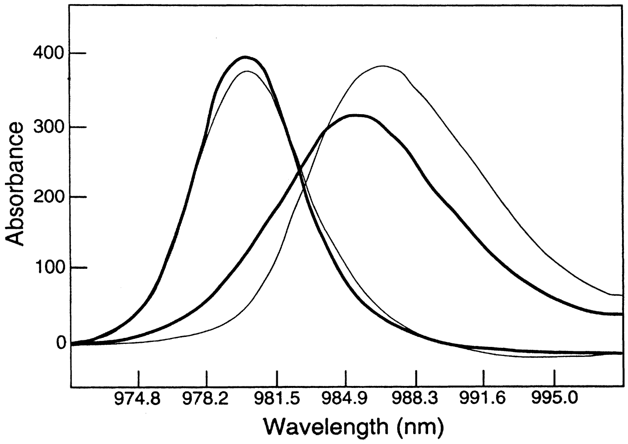

Fig. 1. Molar absorptivity vs. wavelength for the NpO_2^+–mellitate species, at pH 5.0 (———), and 7.5 (———); I=1.0 M.

Table 3
'Apparent' stability constants

Ligand	log β^{app}							
pH:	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5~
Mellitate	1.79	1.92	2.25	2.32	2.30	2.34	2.35	2.34
Pyromellitate	—	—	—	—	1.77	—	—	—
Hemimellitate	1.15	—	2.11	—	2.40	—	—	—
Trimellitate	1.30	—	—	—	1.55	—	—	—
Phthalate	0.91	—	—	—	1.60	—	—	—

T=25°C; I=1.0 M ($NaClO_4$).

The stability constants were calculated from the 512 data points of the spectra by the program TAFIT [7]. In order to calculate the error within each set of spectra, TAFIT was run with all possible subsets of each run, a subset consisting of all the spectra minus one. When the error of a subset was found to be less than half that of the whole set, the omitted spectrum was eliminated and the process repeated. Theoretical spectra were generated using the concentrations and molar absorptivities calculated by TAFIT for the species of each spectrum, incorporating the standard deviation for each point. The stability constants were recalculated using these theoretical spectra in the data set. The difference between the calculations from the actual and the theoretical spectra provided an uncertainty of ±0.01 in log β^{app}. The 'apparent' stability constants, β^{app}, calculated with the total noncomplexed concentrations, $[L]_T$, of the ligands (i.e. $=[L^{2-}]+[HL^-]+[H_2L]+\dots$) are listed in Table 3.

Table 2
Parameters of the resolved spectral peak for NpO_2L^-

	Mellitate								Pyromellitate	Hemimellitate		Trimellitate		Phthalate	
pH:	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	6.0	5.0	6.0	4.0	6.0	4.0	6.0
$\Delta\lambda$ (nm)	5.3	5.6	5.6	6.0	6.3	6.4	6.7	6.7	5.1	7.5	7.7	3.9	4.9	5.3	5.3
FWHM (nm)	8.9	9.0	9.7	9.7	9.7	9.9	10.0	9.8	8.2	9.0	9.3	8.3	7.8	7.3	8.0

Table 4
Corrected stability constants for NpO_2L

Ligand	n	$\log \beta_{101}$	$\log \beta_{111}$	$\log \beta^{c}_{101}$
Mellitate	6	2.34±0.01	2.2±0.1	1.56
Pyromellitate	2	1.80±0.01	—	1.50
Hemimellitate	2	2.44±0.02	1.2±0.2	2.14
Trimellitate	1	1.57±0.02	−1.3±0.2	1.57
Phthalate	1	1.62±0.02	0.4±0.2	1.62

$T=25°\mathrm{C}$; $I=1.0$ M ($NaClO_4$).

$$\beta^{\mathrm{app}} = \frac{([\mathrm{ML}]+[\mathrm{MHL}]+[\mathrm{MH_2L}])}{[\mathrm{M}][\mathrm{L}]_{\mathrm{T}}}$$

The stability constants, β_{1n1} ($n=0$, 1) of the individual complexed species were calculated from the β^{app} values, and the concentrations of the anions determined with the dissociation constants in Table 1. Resolution of the β^{app} values was accomplished using the relationship:

$$\beta^{\mathrm{app}} = \beta_{101} \cdot f_0 + \beta_{111} \cdot f_1 + \beta_{121} \cdot f_3$$

where f_i is the fractional concentration ($f_i=[\mathrm{H}_i\mathrm{L}/[\mathrm{L}]_{\mathrm{T}}$, $i=0$, 1, 2). Values of β_{101} and β_{111} could be calculated from the variation of β^{app} and f_i except for pyromellitate, for which only one pcH system was measured. The values of β_{101} and β_{111} are listed in Table 4. The values of β_{102} were not sufficiently reliable to list. The values of β_{101} and β_{111} in Table 4 indicate that protonation of non-bonding carboxylate groups results in little perturbation of the β values.

4. Discussion

The ligands studied use two neighboring carboxylate groups to form chelates with the neptunyl ion. The number, n, of possible chelating binding sites are given for each ligand in Table 4. The stability constants listed in Table 4 were corrected for the differences in probability of interaction due to the different values of n, the statistical effect, by dividing the stability constant by n, the number of chelating binding sites (i.e. β/n). The values of the statistically corrected stability constants, $\log \beta^{c}_{101}$, are listed in Table 4.

For all of the ligands except hemimellitate, the values of $\log \beta^{c}_{101}$ are in the range 1.5–1.6. The noncomplexing groups of trimellitate, pyromellitate, and mellitate apparently exert very little, if any, influence on the chelating groups and these ligands have approximately the same binding strength as phthalate, once the statistical effect is removed.

A modified Born equation [8] has been used to calculate the effective net charge of the anions in actinide complexes [9]. Using this equation and the corrected stability constants (β^{c}_{101}), the ligand anionic charges were calculated. All the values of Z(L) exceed unity, supporting a chelate nature for the bonding ($Z\sim-1.5$ for all but the hemimellitate ligand which was ~-1.7). To explain the somewhat stronger bonding of the hemimellitate complex and the almost constant bonding in the other complexes, we can consider the possible inductive and/or resonance effects in these bonded aromatic ligands.

Four of the ligands, trimellitate, pyromellitate, hemimellitate, and mellitate, could allow higher negative charge on the chelating carboxylate groups in resonance structures. The presence of increased stability due to this higher chelating group charge should be reflected in the $\log \beta$ values of the ligands when compared to that of phthalate, since the phthalate donor sites cannot have a resonance enhanced charge. However, except for hemimellitate, no increased stability, relative to phthalate, is seen in the statistically corrected stability constants. Resonance places certain steric requirements on the aromatic ring and its substituent carboxylate groups. The ring and the carboxylate C–O bonds must lie in approximately the same plane so that the p orbitals of the aromatic ring and those of the carboxylate oxygens can overlap to form a continuous π system. This places the carboxylate oxygens very close to each other. The positive charge of the cation could serve to reduce repulsion between the chelating oxygen atoms, but not between the non-complexing carboxylate oxygens. The bonding energy of chelation would have to be sufficiently greater than the increased repulsion of the non-complexing carboxylate groups to stabilize the resonance structures. The values of β^{c} in Table 4 indicate this is not the situation (except, possibly, for hemimellitate).

Involving inductive effects would eliminate the necessity to have all of the carboxylate groups coplanar with the aromatic ring. The distance of the non-complexing carboxylate groups from the chelating groups (or the number of bonds between these two) would be the primary consideration, since inductive effects fall off rapidly as a function of distance. On the basis of an inductive effect, hemimellitate and mellitate, ligands with carboxylate groups *ortho* to the two chelating carboxylate groups, would be expected to form the strongest complexes with NpO_2^+. The close proximity of these non-bonding carboxylate groups makes it more likely that electron density would be transferred to the chelating oxygen atoms through induction. However, the question remains why, if there is an increase in the stability of the neptunyl–hemimellitate complex due to inductive effects, is there not an equal or greater increase in stabilization for the neptunyl–mellitate complex.

The mellitate complex could be strengthened by the inductive transfer of electron density from the *ortho* carboxylates but weakened by other factors. For example, we can envision a structure in which one oxygen atom from each of the two carboxylate groups that participate in chelation is attracted more strongly to the cation, causing the carboxylate groups to tilt at an angle towards each other. The neighboring carboxylates would also have to be tilted at a similar angle to minimize the repulsion of their two oxygen atoms. In the case of mellitic acid, this would require the two carboxylate groups *para* to the chelating group to approach each other as closely as the complexing carboxylates, but without the aid of a stabilizing positive charge. This results in an energetically unfavorable structure for mellitate. By contrast, the single non-complexing carboxylate group of hemimellitate could rotate freely to a position that maximizes the distance between its oxygens and those of the neighboring carboxylate group. Accordingly, there would be less steric strain in NpO_2^+–hemimellitate compared to NpO_2^+–mellitate, resulting in a more stable complex due to the inductive effect.

5. Conclusions

These results show that the statistical effect related to the number of potential binding sites plays a significant role in the NpO_2^+–benzenepolycarboxylate binding strength. These aromatic ligands showed no enhanced binding that could be attributed to resonance effects, but there is indication in the hemimellitate binding of enhancement due to an inductive effect.

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