Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Investigations of "Cation–Cation" Complexes of NpO_2^+ Solutions by Large-Angle X-ray Scattering

B. GUILLAUME,[1] R. L. HAHN,* and A. H. NARTEN

Received March 25, 1982

The technique of wide-angle X-ray scattering has been used for the first time to study cation–cation complexes in perchlorate solutions of NpO_2^+ and UO_2^{2+}. Evidence was found in the radial distribution functions of solutions containing both Np(V) and U(VI), or concentrated (1.7 M) Np(V) alone, for a peak at 4.2 Å. This peak is interpreted as being the average nearest-neighbor distance between the actinide ions in solution, showing that they are chemically associated in a stable complex. The result for the 1.7 M Np(V) solution provides independent confirmation of the recent claim of Guillaume, Begun, and Hahn, based on Raman scattering, that a dimer of Np(V) exists in a concentrated solution. While providing corroboration for the existence of complexes of Np(V) with U(VI) and of Np(V) with Np(V), in solution, the present data are insufficient to define their structure unambiguously.

Introduction

Since their discovery by Sullivan et al. in 1961[1] several different techniques have been used to study the cation–cation complexes of pentavalent actinides; these methods include absorption spectrophotometry,[2-8] proton spin relaxation,[2] potentiometry,[2] electron paramagnetic resonance,[8] infrared spectroscopy,[4] and Mössbauer spectroscopy.[9] Yet, despite these efforts, disagreement[5-8] still exists in the literature concerning the detailed characteristics and structures of these unusual species in solution; there have even been some questions raised about the very existence of these complexes (see, e.g., ref 5–8).

Recently, we have begun to apply the techniques of Raman spectroscopy and X-ray scattering, which were previously not used in this context, to the study of such complexes of NpO_2^+. The Raman spectra showed changes in the characteristic ν_1 stretching vibrational transition of Np–O when the Np concentration was increased above 0.2 M or when other multivalent ions, such as UO_2^{2+}, were added to the solution. These Raman studies confirmed the existence of the previously claimed Np(V)–U(VI) complex in perchlorate medium and presented evidence that a new complex, a dimer of Np(V), also exists.[10]

Done concurrently with our Raman investigations, the wide-angle X-ray scattering studies reported in this paper were initiated to look for a definite geometrical relation between the heavy-element components of the cation–cation complexes. If evidence for a characteristic nearest-neighbor distance between actinide atoms could be found in the measured pair distribution functions, the result would provide corroboration for the stable association of two or more actinide ions in a complex. As is shown in the present work, such evidence was found for the association of Np(V) with U(VI) and of Np(V) with Np(V) to form a dimer in concentrated solution.

Experimental Section

Chemicals. The ^{237}Np that was used was obtained as the dioxide from the Oak Ridge National Laboratory. The neptunium(V) perchlorate solutions were obtained by dissolution of NpO_2 in nitric acid and then fuming to dryness with perchloric acid. The residue was heated and melted to eliminate excess acidity. A mixture of Np(VI) and Np(V) was obtained, and after dissolution in water, electrolysis at controlled potential was used to obtain pure Np(V). Partial evaporation to concentrate the solutions was performed at 50 °C under nitrogen. The maximum concentration obtained for stable solutions of neptunium(V) perchlorate, at 25 °C, was 3 M. The uranium(VI) perchlorate solution was prepared by fuming uranyl nitrate to dryness with concentrated $HClO_4$ and taking up the residue with water.

The neptunyl solutions were standardized by conventional radiometric and spectrophotometric measurements. The uranium stock solution was analzyed by the ORNL Analytical Chemistry Division. The low concentration of free acid was obtained by pH potentiometric titration with NaOH in the presence of large amounts of fluoride ion.

Five different solutions containing a variety of concentrations of either NpO_2ClO_4, $UO_2(ClO_4)_2$, or both of these compounds were prepared. ClO_4^- ion was used because of its weak complexing ability. All of the solutions were acidic, with $HClO_4$ concentrations varying from 0.07 to 0.2 M. Because the cation–cation complexes are weak, i.e., the K/Γ equilibrium values are ~3 for the Np(V)–U(VI) complex and 0.8 for the Np(V) dimer,[10] fairly concentrated solutions, varying in total actinyl ion (AnO_2^{m+}) concentration from 0.5 to 2.5 M, were used in the X-ray-scattering experiments. The compositions of the solutions are listed in Table I.

X-ray Scattering. The wide-angle X-ray-scattering apparatus and its use have been extensively described previously.[11] The variation of the intensity of the scattered Mo Kα X radiation (λ = 0.7107 Å) with angle was measured in reflection geometry in four angular ranges, extending from 2 to 130°.

A specially sealed polyethylene cell was constructed to minimize the hazard of radioactive contamination by the hundreds of milligrams of neptunium in the samples and to provide proper containment of minimal amounts of the concentrated solutions. Because of the large mass absorption coefficients of Np and U (42 and 97 cm^2/g, respectively), very shallow samples of solution could be used in the scattering experiments. The container thus was designed to hold a volume of solution of ~1–2 mL, with a depth <2 mm, while exposing a flat surface area of ~3 cm^2 to the X-ray beam.

Results and Discussion

The intensity of scattered radiation was corrected for contributions from background radiation, polarization, absorption, and multiple and Compton scattering.[11] A fluorescence correction for uranium was also made. From the corrected angular distributions, a structure function

$$H(k) = [S(k) - \sum_\alpha f_\alpha^2(k)]/[\sum_\alpha f_\alpha(k)]^2$$

was derived, where $S(k)$ is the coherent scattering function, $f_\alpha(k)$ is the coherent scattering length[12] of atom α, and k =

---

[1] Guest scientist on assignment from the Centre d'Etudes Nucléaires, Departement de Genie Radioactif, Fontenay-aux-Roses, France.

[2] J. C. Sullivan, J. C. Hindman, and A. J. Zielen, *J. Am. Chem. Soc.*, **83**, 3373 (1961).

[3] (a) J. C. Sullivan, *J. Am. Chem. Soc.*, **84**, 4256 (1962); (b) J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).

[4] R. K. Murmann and J. C. Sullivan, *Inorg. Chem.*, **6**, 892 (1967).

[5] A. A. Frolov and A. G. Rykov, *Radiokhimiya*, **16**, 556 (1974).

[6] A. G. Rykov and A. A. Frolov, *Radiokhimiya*, **14**, 709 (1972).

[7] A. G. Rykov and A. A. Frolov, *Radiokhimiya*, **17**, 187 (1975).

[8] C, Madic, B. Guillaume, J. C. Morisseau, and J. P. Moulin, *J. Inorg. Nucl. Chem.*, **41**, 1027 (1979).

[9] D. G. Karraker and J. A. Stone, *Inorg. Chem.*, **16**, 2979 (1977).

[10] B. Guillaume, G. M. Begun, and R. L. Hahn, *Inorg. Chem.*, **21**, 1159 (1982).

[11] A. H. Narten and H. A. Levy in "Water, A Comprehensive Treatise", Vol. I, F. Franks, Ed., Plenum Press, New York, 1979, p 311.

[12] Scattering factors and dispersion lengths were taken from "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

0020-1669/83/1322-0109$01.50/0 © 1983 American Chemical Society

Table I. Solutions Used in X-ray-Scattering Experiments

soln no.	$[NpO_2ClO_4]$, M	$[UO_2(ClO_4)_2]$, M	$[HClO_4]$, M	ρ_0, Å^{-3}	$[NpO_2^+]$,[a] M	$[UO_2^{2+}]$,[a] M	[complex],[a] M
1	0.50	0.50	0.068	0.0373	0.29	0.29	0.21
2	0.81	1.71	0.109	0.0437	0.15	1.05	0.66
3	1.70	0	0.23	0.0390	0.96	0	0.37
4	0.50	0	0.068	0.0351	0.38	0	0.06
5	0	0.50	0.068	0.0368	0	0.50	0

[a] Concentrations of the free AnO_2^{m+} ions and of the cation–cation complex were calculated from the equilibrium K/Γ values given in ref 10.

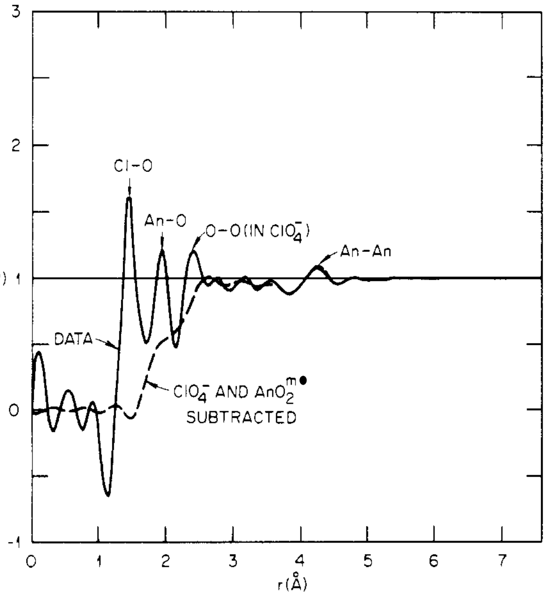

Figure 1. Radial distribution function, $G(r)$, for the 1.7 M solution of NpO_2ClO_4 (solid curve). Contributions of ClO_4^- and AnO_2^{m+} ions have been subtracted in the dashed curve.

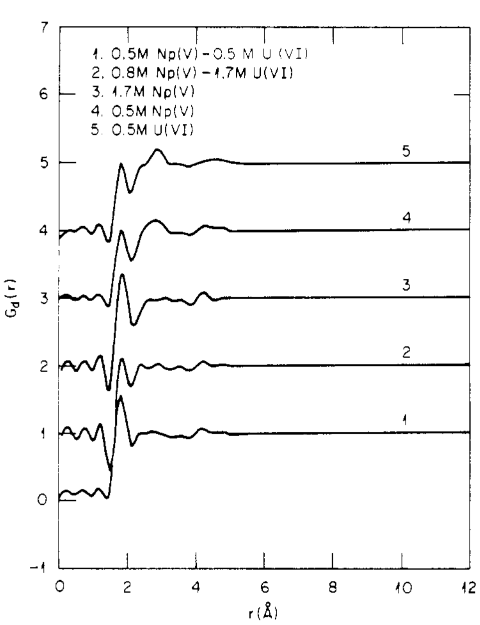

Figure 2. $G(r)$ functions for all five of the solutions studied (see Table I). Contributions due to the ClO_4^- ion have been subtracted.

$(4\pi/\lambda)\sin\theta$, with 2θ being the scattering angle. The structure function was then Fourier transformed to give

$$G(r) = 1 + (2\pi^2\rho_0 r)^{-1}\int_0^{k_{\max}} k\,H(k)\sin(kr)\,dk$$

where ρ_0 is the number density/Å^3 of scattering centers in the solution and $G(r)$ is the radial distribution function (RDF).

An example of the experimental $G(r)$ functions determined in this work, that of the 1.7 M solution of NpO_2^+ (solution 3), is shown in Figure 1. The prominent features observed in this RDF are the peaks at 1.4, 1.8, 2.3, and 4.2 Å. The peak at 1.8 Å is assigned to the metal–oxygen distances in U=O and Np=O on the basis of the agreement with the bond lengths measured in single crystals containing the linear UO_2^{2+} and NpO_2^+ ions.[13,14] The peaks at 1.4 and 2.3 Å are assigned to the Cl–O and O–O distances in the tetrahedral ClO_4^- ion on the basis of studies of $LiClO_4$ solutions.[15] Contributions from metal–oxygen interactions in the equatorial plane of the AnO_2^{m+} ion such as those due to hydration, An–OH_2, are possibly also included in the 2.3-Å peak.

No evidence for +,– ion pairs such as An^+,Cl^- is observed in the RDF; this interaction should be weak and should occur at large distances, >5 Å, given the weak complexing ability of ClO_4^- ion in solution. The low-intensity ripples seen below 1.2 Å are unphysical, being caused by the cutoff in the experimental data at $k = 16$ Å^{-1}.

The peak at 4.2 Å is not characteristic of any of the distances in the free actinyl ion (AnO_2^{m+}) nor of those in the perchlorate ion. This fact is evidenced by the observation that the peak is not altered when the known contributions of the free actinyl ion and the perchlorate ion are subtracted from the RDF in Figure 1.

Figure 2 shows the net $G(r)$ functions for all five of the solutions that we studied by X-ray scattering, the contributions due to the ClO_4^- ions having already been subtracted.[15] The following observations can be made about these RDF curves: (1) Solution 5, which contains only 0.5 M UO_2^{2+}, shows a weak, broad band centered at 4.7 Å but no structure at 4.2 Å. (2) Solutions 1–4, which contain Np(V) in concentrations ≥0.5 M, show structure at 4.2 Å. (3) Solution 1, containing 0.5 M each of Np(V) and U(VI), has a more defined peak at 4.2 Å than does solution 4, which contains 0.5 M Np(V) only. (4) As the Np(V) concentration increases, the intensity of the 4.2-Å peak also increases.

On the basis of these observations, we interpret the 4.2-Å peak as representing the nearest-neighbor distance between the actinide atoms in the cation–cation complex. It is known that U(VI) in acidic medium exists only as the free UO_2^{2+} ion. Thus, no peak at 4.2 Å should be observed. Mixtures of Np(V) with U(VI) are known to give spectroscopic evidence for a cation–cation complex.[8,10] The presence of the 4.2-Å peak in the RDF's of solutions 1 and 2, containing both Np(V) and U(VI), provides independent confirmation of the existence of this complex.

Noteworthy are the $G(r)$ functions for pure Np(V), solutions 3 and 4. When these X-ray studies were begun, evidence had not yet been obtained in our Raman investigations[10] for the existence of a dimer of NpO_2^+ in concentrated solutions. It was thus initially anticipated that a pure solution of Np(V), independent of its concentration, would not show evidence for a cation–cation complex. Yet a clear peak is seen at 4.2 Å in the RDF of solution 3, for 1.7 M Np(V). This result thus

---

(13) J. H. Burns and C. Musikas, *Inorg. Chem.*, **16**, 1619 (1977).
(14) M. Åberg, *Acta Chem. Scand.*, **23**, 791 (1969).
(15) A. H. Narten, unpublished data.

corroborates the claim made in the Raman work of the existence of the Np(V) dimer.[10] Since the dimer forms at Np(V) concentrations $\gtrsim$0.2 M, solution 4, with 0.5 M Np(V), should also display a peak at 4.2 Å, albeit much smaller than that seen for solution 3.

Equilibrium constants, K/Γ, for the Np(V)–U(VI) complex and Np(V) dimer were determined by us in ref 10. The concentrations of actinyl ions and the cation–cation complex for solutions 1–5 were calculated with these K/Γ values. We note that there is a qualitative correlation between the relative intensities of the peaks at 1.8 and 4.2 Å and these calculated concentrations, as listed in Table I. Because the intensities of the peaks in the $G(r)$ functions are small, their dependene upon the concentration of the complex cannot be established quantitatively.

Another point of interest concerning the radial distribution functions in Figure 2 is that the association of water molecules in the solution—the so-called "water structure", as exemplified by the O–O intermolecular water–water distance at 2.9 Å—is seen in solutions 4 and 5, which contain only $Np_2O_2ClO_4$ or $UO_2(ClO_4)_2$ at relatively low concentrations, 0.5 M. This feature of the $G(r)$ function is not seen in solutions 1–3. It may be that the presence of the cation–cation complex or the high concentrations of ClO_4^- ion disrupt this feature of aqueous solutions.

It is noteworthy that the actinide–actinide distance that we find, 4.2 Å, is comparable to the value of 3.9 Å reported as the U–U distance for solutions and solids containing polymers of hydrolyzed UO_2^{2+} species.[14,16,17] A point of distinction between the two sets of results is that the uranium atoms in the polymers are joined by OH^- bridges, while the cation–cation complexes are formed in strongly acidic media, where hydrolysis is not possible. The large distance, 4.2 Å, does indicate that the metal ions are not directly bonded to each other. This distance, along with the 1.8-Å value for An–O, does not define a unique structure for the actinide cation–cation complex. As discussed in ref 10, at least two models have previously been suggested for the complex, in which the actinide ions are linked either via the axial oxygen of the actinyl(1+) ion or through the oxygen atom of some ligand such as ClO_4^- or H_2O. Both models are consistent with our data. Thus, while the present work has provided supporting evidence for the existence of the cation–cation complexes, further studies are required to define their structure.

Acknowledgment. This work was sponsored by the Divisions of Chemical Sciences and Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corp., and by the Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France. We wish to thank J. S. Johnson for suggesting this experimental approach to B.G. and R.L.H. and acknowledge C. F. Baes and J. H. Burns for interesting discussions about this subject. B.G. wishes to thank the Chemistry Division of Oak Ridge National Laboratory for the hospitality received during his stay and the Centre d'Etudes Nucléaires of Fontenay-aux-Roses for support while this project was carried out at ORNL.

Registry No. $NpO_2(ClO_4)$, 83477-23-0; $UO_2(ClO_4)_2$, 13093-00-0.

---

(16) M. Åberg, *Acta Chem. Scand.*, **24**, 2901 (1970).

(17) C. Musikas and A. H. Narten, *Inorg. Nucl. Chem. Lett.*, **14**, 283 (1978).

Contribution from the Molecular Research Institute, Palo Alto, California 94304, and
the Extraterrestrial Research Division, NASA-Ames Research Center, Moffett Field, California 94035

Interaction of Metal Ions and Amino Acids: Possible Mechanisms for the Adsorption of Amino Acids on Homoionic Smectite Clays

ABHA GUPTA, GILDA H. LOEW,* and JAMES LAWLESS

Received February 17, 1982

In this study the binding of amino acids to hexahydrated Cu^{2+} and Ni^{2+} ions, a process presumed to occur when they are adsorbed in the interlamellar space of homoionic smectite clays, has been characterized by using a semiempirical molecular orbital method. For the investigation of both metal ion and amino acid specificity in binding, five α-amino acids, α-alanine, valine, sarcosine, α-aminobutyric acid, and α-aminoisobutyric acid, as well as β-alanine and γ-aminobutyric acid were included. The α-, β-, and γ-amino acids were assumed to bind as bidentate anionic ligands, forming either 1:1 or 1:2 six-coordinated five-, six-, and seven-membered-ring chelate complexes, respectively. Energies of complex formation, optimized geometries, and electron and spin distributions were obtained; and steric constraints of binding of the amino acids to the ion-exchanged cations in the interlamellar spacing of a clay were examined. The results of these studies suggest that hexahydrated Cu^{2+} forms more stable complexes than hexahydrated Ni^{2+} with all the amino acids studied. Among these amino acids, complex formation does not favor the adsorption of the biological subset. Calculated energetics of complex formation and steric constraints predict that 1:1 rather than 1:2 metal–amino acid complexes are generally favored in the clay. Calculated spin densities for these two types of complexes suggest that electron spin resonance techniques can be used to further verify this prediction.

Introduction

It has been proposed that a crucial step in the origin of life was the formation of important biopolymers from the simple organic molecules contained in the primitive atmosphere. Among many aspects of prebiotic synthesis under consideration is the possible prebiological role of clay surfaces, first suggested by Bernal,[1] in processes such as selection and concentration of key monomers from dilute aqueous solution and their subsequent condensation to bipolymers.[2-11] In particular, the

---

* To whom all correspondence should be addressed at the Molecular Research Institute.

(1) Bernal, J. D. "The Physical Basis of Life"; Routledge and Kegan Paul: London, 1951.

(2) Paecht-Horowitz, M.; Berger, J.; Katchalsky, A. *Nature* (*London*) **1970**, *228*, 636.

© 1983 American Chemical Society