

that the molten transition metal is involved in the excitation and the transport of carbon. No extension of these remarks to the formation of natural diamond is possible at present.

Acknowledgments.—I wish to thank E. T. Conlin and W. Mowrey for extensive experimental assistance. G. Schacher (General Engineering Laboratory, General Electric Company) provided

access to a suitably sensitive mass spectrometer. This work has received the benefits of discussion with F. P. Bundy, H. M. Strong and R. H. Wentorf, Jr., all of this laboratory and co-discoverers (with H. T. Hall) of the original diamond synthesis procedure, and with R. W. Guard, Metallurgical Products Dept., General Electric Co., Detroit, Mich.

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Complex Ion Formation between Cations. Spectra and Identification of a Np(V)-Cr(III) Complex^{1,2}

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RECEIVED APRIL 14, 1962

A complex ion $\text{Cr}(\text{H}_2\text{O})_6^{+3}(\text{NpO}_2^+)$ has been separated by use of an inorganic ion exchanger. Identity of the species was determined by the analytical ratio of Np/Cr in solution. Spectra are presented. Specific rate for decomposition of the complex is $(2.32 \pm 0.08) \times 10^{-6} \text{ sec.}^{-1}$ at 25° in 1.0 *M* HClO₄. From spectrophotometric observations the relative strength of interaction between Np(V) and M(III) perchlorates in 2.0 *M* HClO₄ is Fe > In > Sc > Ga > Al.

Although the vibronic transitions of the Np(V) ion in aqueous media are not markedly influenced by anions such as sulfate or chloride they are strongly affected by some cations. We have demonstrated³ that the association quotient for the reaction between Np(V) and U(VI) obtained from spectrophotometric data is in excellent agreement with the value obtained from potentiometric measurements carried out in acidic perchlorate media with the weighted mean value at 25° and ionic strength of three; $K = 0.690 \pm 0.013 \text{ l./mole}$.

To provide additional information on the structure of such complex species a Np(V)-Cr(III) complex has been prepared, separated from the reaction mixture and its spectrum characterized. In an effort to determine the importance of the factors which influence association between Np(V) and cations in perchloric acid-perchlorate solutions, spectrophotometric observations have been made on solutions of a number of di-, tri- and tetravalent salts.

Experimental

Solution.—The preparation and standardization of stock solutions of perchloric acid, sodium, Np(V), yttrium, lanthanum, thorium,⁴ mercurous and mercuric⁵ perchlorates have been described elsewhere. Solutions of aluminum, scandium, gallium, indium, silver, lead and bismuth perchlorates were prepared by the dissolution of the appropriate oxide in reagent grade perchloric acid followed by recrystallization if feasible. Solutions of ferric perchlorate were prepared from G. F. Smith Co. ferric perchlorate that had been twice recrystallized from concentrated perchloric acid. Prior to the first recrystallization a small amount of hydrogen peroxide was added to the solution to insure that the iron was fully oxidized.⁶ Chromic perchlorate solutions prepared by the double recrystallization of G. F. Smith

material and by the method of Postmus and King⁷ gave identical results in kinetic studies. On the basis of the criteria presented by Altman and King⁸ both preparations were relatively free of polymeric Cr(III) species with values for $\epsilon_{230}/\epsilon_{260}$ of 0.55 and 0.20, respectively.

Conventional methods of analysis were used by the analytical division of this laboratory to standardize the above stock solutions. Np(V) concentrations were determined by radiometric assay.

Ion Exchange Separations.—Initial runs were made at room temperature using columns of 1 cm. diameter and *ca.* 10 cm. length of Dowex 50 cation exchanger (AG 50W-X 12) 200–400 mesh in the hydrogen ion form. The resin used had been previously treated with perchloric acid then washed extensively with triple distilled water. Final separations were achieved by use of an inorganic exchanger Bio-Rad ZP-1, 100–200 mesh (Bio-Rad Laboratories). This zirconium phosphate type of cation exchange crystal was washed with perchloric acid and triple distilled water prior to use. The separation was carried out in a jacketed column with the temperature maintained at 0–1°.

Spectrophotometric Procedures.—A Carey Model 14 MR Recording Spectrophotometer, with cell compartment thermostated at 25°, was used for all spectral studies. 1, 2 and 5 cm. quartz absorption cells were used. Detailed procedures used in the spectrophotometric studies have been previously described.³ For the Np(V)-Cr(III) complex perchloric acid of the appropriate molarity was used to determine necessary blank corrections. With the exception of the chromic perchlorate solutions the spectra obtained as soon as possible after mixing did not change over a period of weeks.

Analysis of Np(V)/Cr(III).—Standard radiochemical assay procedures were used to determine the Np(V) concentration. Chromium concentrations were determined using the method described by Gates and King⁹ after destruction of the complex by zinc amalgam.

Results

A solution originally 2.0 *M* in chromic perchlorate, 1.0 *M* perchloric acid and *ca.* 10^{-8} *M* in neptunium(V) perchlorate when examined spectrophotometrically shows a slow decrease in the optical density at 9800 Å. and concomitant increase at 9937.5 Å. At 25° the spectrum ceases to change after several days and remains constant over a period of months.

(7) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1209 (1955).

(8) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2826 (1961).

(9) H. S. Gates and E. L. King, *ibid.*, **80**, 5012 (1958).

(1) Work performed under the auspices of the United States Atomic Energy Commission.

(2) A preliminary account of this work presented at the 7th International Conference on Coordination Chemistry, Stockholm, June 1962.

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

(4) J. C. Sullivan, A. J. Zielen and J. C. Hindman, *ibid.*, **82**, 5288 (1960).

(5) A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, in press.

(6) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

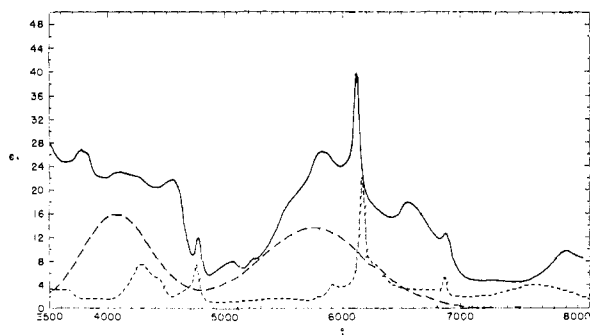


Fig. 1.—Absorption spectra of Np(V)·Cr(III) —, Cr(III) — —, Np(V) - - -.

If we prepare a solution 1.31 *M* in Cr(III), 1.0 *M* HClO₄ and 0.142 *M* in Np(V), allow it to equilibrate for several weeks and examine an aliquot of this solution (in molar perchloric acid) spectrophotometrically we again observe peaks at 9800 and 9937.5 Å. Over a period of days the optical density at the latter wave length decreases with an increase at 9800 Å.

Since it is known that the water molecules in the first coordination sphere of the chromic ion exchange slowly with solvent water, these observations lead to the hypothesis that we are obtaining an "inner sphere" complex. A test of this hypothesis is to separate the complex from the reaction mixture.

Separation Experiments.—After the appropriate preliminary experiments an aliquot of the second reaction mixture described above was adsorbed at the top of a column of Dowex-50. The Np(V) was readily eluted with 1 *M* HClO₄, and the Cr(III) with 2.5 *M* HClO₄.¹⁰ A blue-green band remained at the top of the column and could not be moved even with 9 *M* HClO₄, 3 *M* La(ClO₄)₃ or 1 *M* Th(ClO₄)₄.¹¹

The procedure finally evolved using the inorganic ion exchanger ZP-1 consisted of elution of the Np(V) and Cr(III) with 7–10 column volumes of 0.1 *M* HClO₄ plus one column volume of 0.5 *M* HClO₄. The complex was collected in 1–2 column volumes of 1.0 *M* HClO₄.

The ratio of Np(V)/Cr(III) in the molar perchloric acid fraction of the eluant for three separate runs was determined to be 1.005 ± 0.023 with individual values of (1.004, 0.993), (0.980, 0.983) and (1.110, 0.986). The values in brackets are for consecutive 1.0 *M* HClO₄ fractions of the same column run.

Spectra of Np(V)–Cr(III) Complex.—Complete spectra of the complex, hydrated chromic and Np(V) ions in molar perchloric acid are presented in Figs. 1, 2 from 3500–11,300 Å. Values for the molar extinction coefficients of the complex (defined in the usual manner)¹² are presented in Table I for the main bands.

(10) E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

(11) These experiments are described to provide a background for the discussion of the separations using the less familiar ZP-1 ion exchanger and merely indicate the presence of a new species in the reaction mixture.

(12) I. A. Christiansen, *J. Am. Chem. Soc.*, **82**, 5520 (1960).

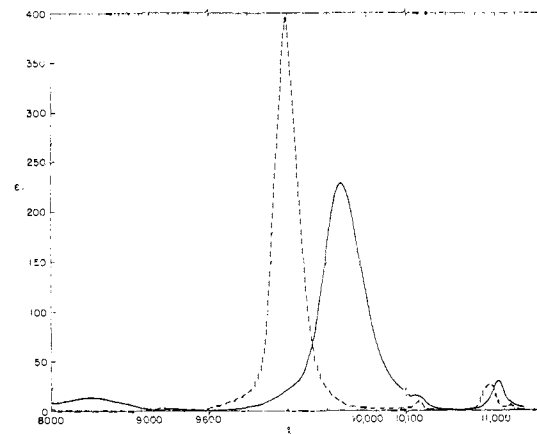


Fig. 2.—Spectra of Np(V) - - - and Np·Cr(III) —.

Kinetic Measurements.—The specific rate k of the reaction $[C] = [Np(V) \cdot Cr(III)] \xrightarrow{k} [Np(V)] + [Cr(III)]$ was determined in 1.0 *M* perchloric acid at 25°. Over a period of time from 1–2 half-lives the reaction followed the rate law $-d[C]/dt = k[C]$, with a value of $k = (2.32 \pm 0.08) \times 10^{-6} \text{ sec.}^{-1}$. This value represents an average of six kinetic runs and the uncertainty is the standard deviation. In five of these experiments the complex was obtained from a column separation, the other from a dilution of the equilibrium mixture previously described. Results obtained from a detailed study on the kinetics of this system will be reported in the near future.

TABLE I
MOLAR EXTINCTION COEFFICIENTS OF Np(V)–Cr(III)
COMPLEX ION BANDS 1.0 *M* HClO₄, 25°^a

$\lambda(\text{Å})$	ϵ	σ	$\lambda(\text{Å})$	ϵ	σ
3775	26.8	1.9	6550	18.0	1.7
4100	23.0	1.8	6875	12.7	1.7
4550	21.7	1.4	7900	9.8	1.3
4775	12.0	0.8	8400	13.8	1.1
5075	8.0	0.5	9937.5	228.4	3.4
5250	8.4	1.0	10200	15.5	2.3
5825	26.4	1.9	11040	29.9	1.6
6115	39.8	1.8			

^a σ is the standard deviation.

Additional Spectrophotometric Observations.—The most characteristic feature of the absorption spectra of Np(V) in aqueous solution is the sharp band centered at 9800 Å. If the solution composition is changed from molar perchloric acid to molar perchloric acid–three molar lanthanum perchlorate the only changes observed are of the type considered as "medium" effects. This type of behavior, which has been previously discussed,³ involves a small change in the wave length at which the maximum occurs (5–10 Å.), a general broadening of the absorption band and a small decrease of the value of the molar extinction coefficient at the maximum.

If we replace the lanthanum perchlorate by stoichiometric amounts of ferric perchlorate, maintaining constant acidity and Np(V) concentration, the optical density at 9800 Å. decreases and a new band centered at 9970 Å. appears with optical

density increasing as the ferric perchlorate concentration increases. Similar effects have been observed with solutions of the tri-valent perchlorates of Al, Ga, Sc and In in perchloric acid.

The wave lengths at which the new bands have a maxima are presented in Table II. Included in the table are values for the apparent molar extinction coefficient at 9800 Å. obtained from a graphical analysis of the spectra.

TABLE II

WAVE LENGTHS OF NEW MAXIMA AND APPARENT MOLAR EXTINCTION COEFFICIENT AT 9800 Å.

2 M HClO₄, 1 M M(III) (ClO₄)₃, 1.4 × 10⁻³ M Np(V) 25°

M(III)	λ(Å.)	ε at 9800 Å.
Al ^a	9890	360
Ga	9910	282
Sc	9940	171
In	9910	90
Fe	9970	52
Cr	9937	22.2 ± 1.5 ^b

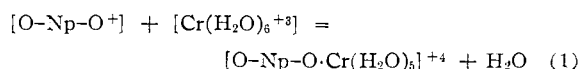
^a Al(ClO₄)₃ = 2.1 M for determination of λ. ^b 1 M HClO₄, ~ 1 × 10⁻³ M Np(V)·Cr(III).

Marked changes from the original Np(V) absorption spectrum are also observed at other wave lengths. For example, in the case of the ferric perchlorate solution, described in Table II, new bands appear at 11025, 8650–8700, 8050, 6850 and 6110 Å. The beginning of the intense band in the ultraviolet region of the Np(V) spectrum shows a pronounced shift towards the red. This can be demonstrated by comparing the value for the apparent molar extinction coefficient of Np(V) in 2.0 M HClO₄, molar in lanthanum perchlorate and a solution at the same acidity molar in indium perchlorate where at 2250 Å. the respective values are 800 and 980.

Cations of charge other than plus three show behavior similar to that discussed for ferric perchlorate. In a solution 0.8 M in thorium perchlorate a new band with a maximum at 9980 Å. is observed. In molar mercurous perchlorate a band with maximum at 9890 Å. appears. A solution 1.7 M in bismuth perchlorate, 2 M in perchloric acid (in which the bismuth is presumably BiO⁺¹³) presents a markedly altered spectrum with the maximum at 9925 Å. When Hg(II) and Pb(II) perchlorates replace magnesium perchlorate in stoichiometric quantities the optical density at 9800 Å. decreases while that at 9900 Å. increases with increasing Hg(II) or Pb(II) concentration. However in the case of these divalent salts two distinct bands are never observed.

Discussion

The experimental observations presented are consistent with the postulated reaction



(13) D. F. Smith, *J. Am. Chem. Soc.*, **45**, 370 (1923).

In terms of the model suggested for the Np(V) ion the bridging between the neptunium and chromium atoms would be *via* an oxygen atom.

In particular the kinetic data shows that this complex is not of the outer sphere type with respect to the primary coordination sphere of Cr(III). While it is reasonable to assume that the final product is formed by substitution at Cr(III) it has been pointed out¹⁴ that the final configuration can also be obtained by substitution at Np(V).

Spectrophotometric observations provide additional evidence that bonding in the complex is *via* O-Np-O·Cr rather than through a water molecule in the equatorial plane of Np(V). In a LiNO₃-KNO₃ eutectic at 160°¹⁵ a spectrum is obtained that is very similar, in position and relative intensity of the absorption bands, to the Np(V) spectrum observed in aqueous solution. This strongly suggests that changes in composition of the coordination sphere outside of the linear O-Np-O entity have little effect on the energy of the electronic transitions characteristic of the Np(V) molecule. Then when pronounced changes in the energy of the electronic transitions are observed, as for example in the region of the spectrum for the complex between 7000–11300 Å., they must reflect changes in the axially symmetrical field¹⁶ of the linear O-Np-O molecule. A reasonable mechanism for such a change would be variation of a neptunium-oxygen bond distance arising from interaction between the chromium and oxygen atoms.

If we assume a model for the Np(V) ion in aqueous solution analogous to that proposed by Connick and Hugus¹⁷ for the uranyl ion it is apparent that classical electrostatic arguments based on point charges are also consistent with the formulation of the complex as O-Np-O·Cr.

Let us assume a distribution of charge between the neptunium and oxygen atoms of +3 and -1, respectively, with the neptunium-oxygen distance 1.9 Å. Results of calculations based on simple electrostatics then indicate that the electric field at a distance of 2.6 Å from one end of the linear (O-Np-O)⁺¹ is essentially zero. It must be emphasized that this oversimplified model is of value only to obviate the necessity of considering gross electrostatic repulsive forces when discussing the complex ion formation and cannot be used as a basis for quantitative understanding of the observations.

In a comparison of the spectrum of the complex with that of its constituents we can recognize the following types of changes: an apparent shift to the red of the original absorption bands, the appearance of bands which are present in neither of the constituents, and increase in intensity of some bands with no change in wave length of the absorption maximum and finally an apparent shift towards the ultraviolet of the narrow band which is

(14) This alternative mechanism has been proposed by Professor H. Taube and one of the referees.

(15) D. M. Gruen, S. Fried, P. Graf and R. L. McBeth, *Proc. Second Intl. Conf. U. N. Peaceful Uses of Atomic Energy*, P/940, Pergamon Press, New York, N. Y., 1959.

(16) J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc. (London)*, **A283**, 20 (1955).

(17) R. E. Connick and Z. Z. Hugus, Jr., *J. Am. Chem. Soc.*, **74**, 6012 (1952).

located at 6160 Å. in the Np(V) spectrum. Simple arguments based on crystal field effects do not appear adequate to interpret these observations.

The changes observed in the original spectrum of Np(V) when cations other than chromic are added to the solution are in themselves considered as evidence for complex ion formation. The results obtained with chromic ion provide additional evidence that such observations indicate the formation of a complex.

If we assume that the values of ϵ at 9800 Å. (presented in Table II) are a measure of the amount of Np(V) that does not interact, these data allow us to order the given set of cations as to the relative strength of their interaction with the Np(V) ion. Such an ordering is presented in Table II where it is evident that Al(III) has the weakest and Fe(III) the strongest interaction.

In addition to the observations presented in the experimental section no evidence was obtained for complex formation between Np(V) and either yttrium (3.0 *M*) or Ce(III), 2.0 *M*, in solutions of the perchlorate salts. This evidently precludes an attempt at a detailed correlation between relative bond strength and other properties characteristic of the trivalent cations such as crystal radii. However we can note that bond formation is observed when such radius is less than or equal to 0.81 Å. and not observed when such radius is greater than or equal to 0.93 Å.

It is apparent that the electronic configuration of the trivalent cation is of importance in the formation of these complexes. This is most clearly demonstrated if we recall that the crystal radii of Ga(III) and Fe(III) are almost equal and note the ordering in Table II. Additional discussion of this point would not be fruitful since, as Jorgensen¹⁸ has pointed out, it is not readily

apparent what importance is to be attached to molecular orbital contributions in bonding of complexes.

Studies of these complexes should provide information which may be of assistance in delineating properties of activated complexes for certain redox reactions. For example in the reduction of Np(V) by V(III)¹⁹ and Np(III)²⁰ the relationship between crystal radii and complex formation is consistent with an inner sphere activated complex in the former and an outer sphere activated complex in the latter reaction.

It is of interest to note that Newton has obtained evidence for the existence of intermediates U(V)·Cr(III)²¹ and Pu(V)·Fe(III)²² during the course of kinetic studies. These intermediates are probably similar to the stable complexes previously discussed between Np(V) and the M(III) ions and suggests that the (O-M-O)⁺ entity (and not detailed electronic configuration of the actinide atom) is the factor most important for the formation of such species.

In addition we may be able to use the Np(V) ion as a probe to increase our understanding of the properties in the first coordination sphere of selected cations. If the spectrum of the Np(V)·Cr(III) complex can be described by theory then comparison of the spectrum obtained with other trivalent cations might be used to obtain relative values for the effective electric field of these ions.

(18) C. K. Jorgensen, Report Xth Solvay Council, Brussels, 1956.

(19) E. H. Appelman and J. C. Sullivan, *J. Phys. Chem.*, **66**, 442 (1962).

(20) J. C. Hindman, J. C. Sullivan and D. Cohen, *J. Am. Chem. Soc.*, **80**, 1812 (1958).

(21) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

(22) T. W. Newton, private communication.

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Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide. IX. *m*- and *p*-Neopentyl Derivatives of Triphenylchloromethane at 0.00°

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RECEIVED JUNE 28, 1962

Analysis of conductance data by Shedlovsky's method provides values of $K_{\text{exp}} = (\text{Ar}_3\text{C}^+)(\text{Cl}^-)/[(\text{Ar}_3\text{CCl}) + (\text{Ar}_3\text{C}^+\text{Cl}^-)]$ of $8.1 \pm 0.5 \times 10^{-4}$ and $3.7 \pm 0.3 \times 10^{-4}$ mole l.⁻¹ and of Λ_0 of 191.5 ± 1.3 and 182.4 ± 3.6 for mono-*p*-neopentyltriphenylchloromethane and di-*m*-neopentylphenylphenylchloromethane, respectively. From values of $K_1 = (\text{Ar}_3\text{C}^+\text{Cl}^-)/(\text{Ar}_3\text{CCl})$, calculated with the aid of Bjerrum's equation, $\Delta\Delta F_1$, measuring the effect of one alkyl group on the work of ionization of trityl chloride, is found to be -1.54 and -0.49 kcal. mole⁻¹ for *p*- and *m*-neopentyl, respectively. Both values are essentially indistinguishable from the corresponding values for methyl. The data for these substituents and for *m*- and *p*-*t*-butyl can be rationalized in terms of joint action of inductive effect and hyperconjugation. They appear to be less consistent with Schubert's "steric inhibition of solvation" model.

Introduction

It has been established in prior papers of this series² that the influence of a substituent attached

(1) Based in part on a portion of a dissertation submitted by Paul E. Rowe in fulfillment of a requirement for the Ph.D. degree, granted by Boston University in June 1959.

(2) Cf., N. N. Lichtin and M. J. Vignale, *J. Am. Chem. Soc.*, **79**, 579 (1957), and earlier papers.

to the aromatic ring on the stability of the triarylcation ion can be evaluated with considerable precision from conductance data. This paper is concerned with the *m*- and *p*-neopentyl groups. Because of our inability to obtain pure crystalline mono-*m*-neopentyltriphenylchloromethane, it was necessary to evaluate the effect of *m*-neopentyl