142. *A Spectrophotometric Study of the Nitrate Complexes of Uranium*(IV).

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The spectra of 0·014M-uranium(IV) solutions in various nitrate–perchlorate media have been determined at $20° \pm 2°$. Isosbestic points observed in different concentration ranges indicate four basic spectra from which the intermediate spectra are compounded. These have been identified as due to (i) U^{4+}, (ii) UOH^{3+}, (iii) UNO_3^{3+}, $U(NO_3)_2^{2+}$ ... etc. (this group give essentially the same spectrum), and (iv) $H_2U(NO_3)_6$. Equilibrium constants for the hydrolysis and nitrate complex-formation of U^{4+} have been determined; those for nitrate complex-formation vary considerably with the total salt concentration in the range 1—4M.

URANIUM(IV) spectra have been measured in three principal ranges of solution: (1) in M-(H,Li)ClO_4 solutions, virtually nitrate-free, in order to determine the first hydrolysis constant of U^{4+}; (2) in 1—4M-(H,Li)(NO$_3$,ClO$_4$) solutions, at an acidity of 1M to suppress hydrolysis; the results show how nitrate complex-formation changes the U^{4+} spectrum, and enable values for the formation constants of the first two complexes to be calculated; and (3) in 5—14M-nitric acid, where the hexanitrato-complex is formed.

Preparation of the solutions required was greatly facilitated by the use of dicæsium hexanitratouranate(IV), Cs$_2$U(NO$_3$)$_6$, which is readily obtained pure and anhydrous and is stable indefinitely in the dark.

The Low-acidity Region.—Kraus and Nelson's studies [1] of the uranium(IV)—uranium(VI) potential and of the absorption spectrum of uranium(IV) in perchlorate solutions have established the existence of the species U^{4+} and UOH^{3+}, which are presumably hydrated, though to an unknown extent. Confirmatory results have now been obtained from measurements on solutions in M-(HClO$_4$ + LiClO$_4$). Parts of the spectra, including the well-defined isosbestic point at 622 mμ, are shown in Fig. 1.

The existence of several isosbestic points supports Kraus and Nelson's conclusion that in such solutions there are only two significant uranium-containing species, U^{4+} and

[1] Kraus and Nelson, *J. Amer. Chem. Soc.*, 1950, **74**, 3901.

UOH^{3+}. From the molar extinction coefficient, ε, at 648 mμ the proportions of the two species can be calculated in the usual way, with the results shown in Table 1.

TABLE 1.

Species present in solution: $[U(IV)] = 0.0114M$; $[H] + [Li] = 1.00M$;
$[NO_3] = 0.07M$; $[ClO_4] = 0.98M$; temp. $20° \pm 2°$.

[H] (M)	ε_{648}	U⁴⁺ fraction	UOH³⁺ fraction	K_c	[H] (M)	ε_{648}	U⁴⁺ fraction	UOH³⁺ fraction	K_c
0.028	34.0	0.515	0.485	0.026	0.254	52.0	0.903	0.097	0.026
0.058	42.0	0.689	0.311	0.026	0.503	53.6	0.938	0.062	0.031
0.105	47.6	0.809	0.191	0.025				Mean 0.027 ± 0.02	

Assumed limiting values of ε_{648}: U⁴⁺ 56·5; UOH³⁺ 10·0.

The equilibrium constant ($K_c = 0.027 \pm 0.02$) was calculated from the formula, $K_c = [UOH^{3+}][H^+]/[U^{4+}]$. Kraus and Nelson found $K_c = 0.027_8$ at 25° in 1·014M-($HClO_4$ + $NaClO_4$), *i.e.*, in a medium closely similar to ours.

The spectra deduced for the U⁴⁺ and UOH³⁺ species are shown in Fig. 4. Identification of the U⁴⁺ spectrum is important in interpreting the results in the following section.

Spectral changes similar to those in Fig. 1 are observed when uranium(IV) is studied in 0·05—0·50M-nitric acid, but are complicated by nitrate complex-formation.

The Intermediate-acidity Region.—Changes also occur in the spectra of uranium(IV) solutions when the concentration of nitrate ion is varied at acidities of $\geqslant$1M, where

TABLE 2.

Molar extinction coefficients of uranium(IV) (0·0114M) in 1—4M-acid at $20° \pm 2°$.

H	Li	Cs	NO₃	ClO₄	ε_{648}	f_A	H	Li	Cs	NO₃	ClO₄	ε_{648}	f_A
		Series 1							*Series 4*				
1·00	Nil	0·02	1·07	Nil	37·0	0·350	1·00	2·00	0·00	0·07	2·98	53·7	0·907
2·00	,,	,,	2·07	,,	30·4	0·130	,,	,,	0·00	0·22	2·83	47·4	0·697
4·00	,,	,,	4·07	,,	26·6	0·033	,,	,,	0·00	0·37	2·68	43·0	0·550
							,,	,,	0·00	0·67	2·38	37·1	0·353
		Series 2					,,	,,	0·00	1·07	1·98	32·1	0·187
1·00	Nil	0·00	0·07	0·98	54·5	0·933	,,	,,	0·00	2·07	0·98	29·0	0·083
,,	,,	0·00	0·15	0·90	52·1	0·853	,,	,,	0·02	3·07	Nil	27·6	0·037
,,	,,	0·01	0·32	0·74	48·5	0·733							
,,	,,	0·01	0·40	0·66	46·0	0·650			*Series 5*				
,,	,,	0·01	0·57	0·49	43·2	0·557	1·00	3·00	Nil	0·07	3·98	54·0	0·917
,,	,,	0·02	0·82	0·25	40·9	0·480	,,	,,	,,	0·17	3·88	47·4	0·697
,,	,,	0·02	1·07	Nil	36·3	0·327	,,	,,	,,	0·32	3·73	41·1	0·487
							,,	,,	,,	0·57	3·49	34·2	0·257
		Series 3					,,	,,	,,	0·82	3·23	32·2	0·190
1·00	1·00	0·00	0·07	1·98	54·7	0·940	,,	,,	,,	1·07	2·98	31·1	0·153
,,	,,	0·00	0·17	1·88	51·0	0·817	,,	,,	,,	1·50	2·48	28·0	0·050
,,	,,	0·00	0·37	1·68	46·2	0·657	,,	,,	,,	2·00	2·05	27·4	0·030
,,	,,	0·00	0·77	1·28	38·9	0·413							
,,	,,	0·00	1·07	0·98	36·2	0·323							
,,	,,	0·01	1·57	0·49	32·5	0·200	Assumed limiting values of ε_{648}: (A) (U⁴⁺) 56·5;						
,,	,,	0·02	2·07	Nil	30·7	0·133	(B) 26·5 (See Fig. 4)						

hydrolysis can be neglected. Fig. 2 shows the spectra obtained for four of the solutions of series 3 of Table 2. Several isosbestic points are observed, the best defined being at 482 and 661 mμ. These isosbestic points are distinct from those discussed in the previous section.

Ermolaev and Krot [2] have also measured extinction coefficients for uranium(IV) in mixed nitrate–perchlorate media. Direct comparisons cannot be made, owing to differences in conditions, but in general their results closely resemble ours. Their choice of experimental conditions did not enable them to observe isosbestic points.

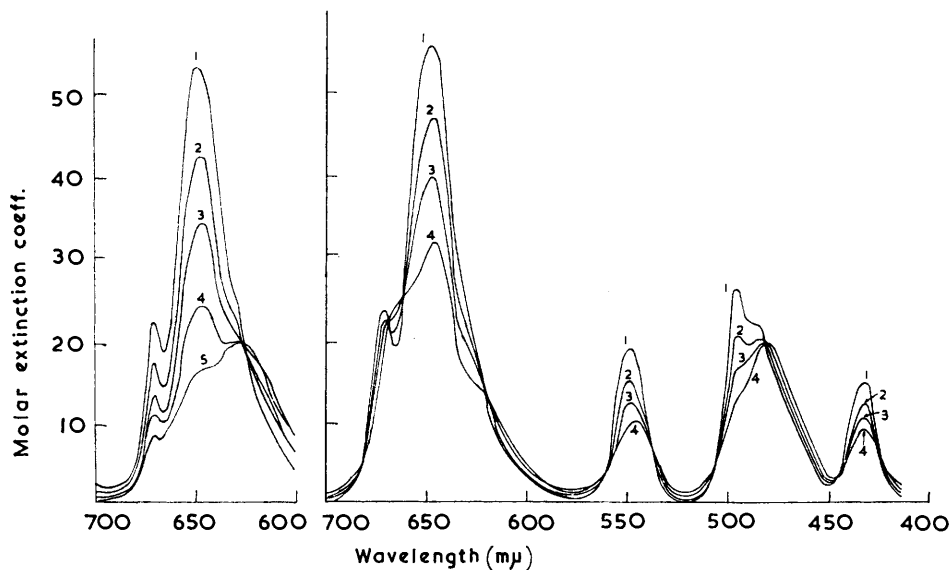[2] Ermolaev and Krot, *Radiokhimiya*, 1962, **6**, 678.

FIG. 1.   FIG. 2.

FIG. 1.   Changes in uranium(IV) spectra due to hydrolysis.
[U(IV)] = 0·0114M;   [NO$_3$] = 0·07M;   [ClO$_4$] = 0·98M;   [H] + [Li] = 1·00M   (except curve 5).   [H] = (1) 0·503, (2) 0·058, (3) 0·028, (4) 0·016, (5) 0·010M [an aqueous solution of Cs$_2$U(NO$_3$)$_6$].

FIG. 2.   Changes in uranium(IV) spectra due to nitrate complex-formation.
[U(IV)] = 0·0114M;   [ClO$_4$] + [NO$_3$] = 2·07M;   [H] + [Li] = 2·0M.   [NO$_3$] = (1) 0·07, (2) 0·37, (3) 0·77, (4), 2·07M.

We might attempt to explain the existence of the isosbestic points on the assumption that we are dealing with mixtures of two species in differing proportions, just as in the low-acidity region.   The results cannot, however, be accounted for so simply.   We can with fair certainty infer the existence of two limiting spectra, which we call A and B; but, whereas spectrum A arises solely from the U^{4+} species, we shall show that contributions to spectrum B come from both UNO$_3$$^{3+}$ and U(NO$_3$)$_2$$^{2+}$, and probably also from U(NO$_3$)$_3$$^+$ and U(NO$_3$)$_4$.

Table 2 gives the extinction coefficient at 648 mμ, and a calculation of the relative proportions of spectra A and B in each case, f_A being the proportion due to A, and f_B (= $1 - f_A$) the proportion due to B.   Similar proportions are obtained from calculations at 496 mμ, but the accuracy is rather lower.

The problem is now to explain the shapes of the f_A–[NO$_3$] curves.   No single equilibrium, U^{4+} + xNO$_3$$^-$ $\rightleftharpoons$ U(NO$_3$)$_x$$^{4-x}$, gives a satisfactory fit, and it is necessary to postulate a series of equilibria, with x = 1, 2, 3 . . ., etc.   According to the usual theory, the successive nitrate complexes are formed in the proportions f_0, f_1, f_2 . . ., etc., where

$$f_0 = 1/X \qquad\qquad \text{U}^{4+}$$
$$f_1 = K_1[\text{NO}_3]/X \qquad \text{UNO}_3{}^{3+}$$
$$f_2 = K_2[\text{NO}_3]^2/X \qquad \text{U(NO}_3)_2{}^{2+}$$
$$\text{etc.} \qquad\qquad \text{etc.}$$

Here we have

$$X = 1 + K_1[\text{NO}_3] + K_2[\text{NO}_3]^2 + \cdots,$$

so that

$$f_0 + f_1 + f_2 + \cdots = 1.$$

The K_n in these formulæ are concentration formation constants, and are only truly constant in a " constant ionic medium," in which activity coefficient changes are negligible. Such a constant medium has, we believe, been sufficiently closely maintained throughout each of the series 2—5 of Table 2, the only major change in each series being the progressive replacement of perchlorate ion by nitrate. Minor changes, *e.g.*, in the residual cæsium concentration, are likely to introduce only second-order effects. We shall, therefore, apply the formulæ just given to each of series 2—5.

As already indicated, the hypothesis that spectrum A is due to U^{4+} and spectrum B to $UNO_3{}^{3+}$, $U(NO_3)_2{}^{2+} \ldots$, etc., is the only one that fits the results in Table 2. This hypothesis involves identifying f_A with f_0, and f_B with $f_1 + f_2 + \cdots$, etc., so that

$$1/f_A = X = 1 + K_1[NO_3] + K_2[NO_3]^2 + \cdots$$

The Mercury computer at A.E.R.E. has been used to express $1/f_A$ as a polynomial in $[NO_3]$, with the results given in Table 3.

TABLE 3.

Results of computation.

Series	K_1	K_2	χ^2/n †	Series	K_1	K_2	χ^2/n †
2	$1\cdot36 \pm 0\cdot07$	0 *	$1\cdot7$	4	$2\cdot30 \pm 0\cdot24$	0 *	$5\cdot2$
	$1\cdot09 \pm 0\cdot10$	$0\cdot49 \pm 0\cdot17$	$0\cdot7$		$1\cdot54 \pm 0\cdot26$	$2\cdot03 \pm 0\cdot57$	$1\cdot7$
3	$1\cdot70 \pm 0\cdot17$	0 *	$5\cdot1$	5	$3\cdot00 \pm 0\cdot48$	0 *	$10\cdot5$
	$1\cdot13 \pm 0\cdot04$	$0\cdot96 \pm 0\cdot06$	$0\cdot1$		$1\cdot44 \pm 0\cdot27$	$5\cdot72 \pm 0\cdot80$	$1\cdot3$

* Zero values assumed for purposes of computation.   † n is number of degrees of freedom.

For each series the first line of results shows the effect of attempting to ignore all complexes but the first; and the second line shows the effect of including both the first and the second complex. The last column gives the χ^2/n test of goodness of fit. The high values of χ^2/n in the first line for series 3—5 tell against an explanation in terms of the first complex only, but a reasonable fit is obtained if the second complex is also included. Attempts to include higher complexes achieved little or no improvement in the χ^2/n values, and gave impossible negative values for some of the K_n. We conclude that contributions from the third and the higher complexes are small at nitrate concentrations up to, say, 3M. K_3 appears to be less than $0\cdot1$.

The standard deviations and the χ^2/n values given in Table 3 are based on assumed errors of $\pm0\cdot002$ in the f_0 values. A further source of error lies in the choice of ε values for the limiting spectra A and B. That for spectrum B is particularly difficult to establish exactly, because there is no uranium(IV) solution, which can be said with certainty to give a pure spectrum B. However, the computation with different values of ε for spectrum B usually gives a rather poorer fit, so we can have some confidence in the ε value chosen. Changing the ε value by $0\cdot5$ unit changes K_1 by ~5% and K_2 by ~15%.

Another complication is incomplete ionisation of the nitric acid. The degree of ionisation may be estimated [3] as 98% throughout our series 2—5, but the exact value is not known and may vary somewhat. Recomputation with the $[NO_3]$ values in Table 2 reduced by 2% tended to raise K_1 by 1—2% and K_2 by ~5%.

Allowing for all the sources of error gives the results in Table 4. They show a rise in both K_1 and K_2 with concentration, and the rather rapid rise in K_2 implies that the contribution from the second nitrate complex increases much more rapidly with concentration than we should expect from a naïve application of the law of mass action.

Alternative explanations of the results, in which the first complex, instead of contributing to spectrum B, either does not contribute at all, or contributes to spectrum A, can be ruled out by considering the function, $F = (1/f_A - 1)/[NO_3]$. On the hypothesis we consider valid, in which the first complex contributes to spectrum B, we have by

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[3] Davis and de Bruin, *J. Inorg. Nuclear Chem.*, in the press.

straightforward algebra, $F = K_1 + K_2[NO_3] + \cdots$. If, however, the first complex does not contribute at all, so that K_1 vanishes, then $F = K_2[NO_3] + \cdots$. If the first complex contributes to spectrum A, so that $f_A = f_0 + f_1$, then:

$$F = (K_2[NO_3] + \cdots)/(1 + K_1[NO_3]).$$

Now plots of F against $[NO_3]$ show that its limiting value at low nitrate concentrations is finite, not zero; and this result is only compatible with the hypothesis adopted here, namely, that the first complex contributes to spectrum B.

Ermolaev and Krot's values [2] are given in Table 4 for comparison. They worked at a rather higher temperature ($26.5°$). Agreement is fair. It must be noted, however, that

TABLE 4.

Overall dissociation constants.

Medium	K_1	K_2	K_3	K_4
Recommended values (this paper)				
1·0M-(H,Li)(NO$_3$,ClO$_4$)	1·1 ± 0·1	0·5 ± 0·2	<0·1	Small
2·0M ,, ...	1·15 ± 0·05	1·0 ± 0·1	<0·1	Small
3·0M ,, ...	1·6 ± 0·3	2·0 ± 0·8	<0·1	Small
4·0M ,, ...	1·5 ± 0·3	6·0 ± 1·4	<0·1	Small
Ermolaev and Krot's values [2]				
2·0M-H(NO$_3$,ClO$_4$)	1·6	1·5	0·96	0·35
2·5M ,, ...	1·6	1·6	1·1	0·49
3·0M ,, ...	1·9	2·0	1·5	0·71
3·5M ,, ...	2·3	3·0	2·6	1·5

Ermolaev and Krot postulate progressive changes in the extinction coefficients on going from the first to the fourth complex, and that this leads to equations with large numbers of variable parameters. The numerical values they find for the K_n are naturally affected and must, moreover, be subject to considerable uncertainty. Our observation of isosbestic points indicates that the extinction coefficients, in fact, vary but little between the first and the fourth complex.

Ermolaev and Krot make no allowance for incomplete ionisation of the nitric acid. This would be more serious in their media than in ours; at their highest acidity ($3.5M$), nitric acid is indeed only 87% ionised.[3] Correcting for this would tend to raise their K_n values.

They also give values for K_3 and K_4, but we feel that these must be treated with considerable reserve, even apart from the issues just raised. The spectrophotometric method is inherently unsuited to determination of K_3 and K_4 because the terms containing them become important only at high nitrate concentrations, and f_A, the quantity measured, is then very small and subject to large errors.

The High-acidity Region.—A third set of isosbestic points is observed for uranium(IV) spectra in 6—14M-nitric acid (Fig. 3), *e.g.*, at 529 and 622 mμ. Again we infer the existence of two limiting spectra, one of which is spectrum B from the intermediate-acidity region. The other, which is fully developed only at the highest nitric acid concentrations and is probably due to a hexanitrato-species, we call spectrum C.

The relative contributions of spectra B and C have been calculated from measurements of extinction coefficients at both 478 and 648 mμ, with the results given in Table 5. As we are not dealing with a constant ionic medium, it is impossible to compute complexity constants from the results. Ryan [4] has obtained similar results to ours in his studies of neptunium(IV) and plutonium(IV); over most of the acidity range, the order of increasing

[4] Ryan, *J. Phys. Chem.*, 1960, **64**, 1375.

Uranium(IV) (0·035M) in 6—14M-nitric acid at 20° ± 2°.

[HNO₃] (M)	6·0	7·0	8·0	9·0	10·0	12·0	14·0
ε_{478}	18·1	17·0	13·1	10·3	8·4	7·1	6·2
ε_{648}	24·3	22·2	17·5	13·0	10·1	66·2	4·4
f_c from ε_{478}	0·058	0·139	0·423	0·586	0·767	0·861	0·927
,, ε_{648}	0·097	0·195	0·400	0·600	0·733	0·902	0·982

Assumed limiting values of ε_{478} and ε_{648} were, respectively, 18·9 and 5·2 for B, and 26·5 and 4·0 for C.

degree of formation of the hexanitrato-complex is Pu(IV) > U(IV) > Np(IV), but above 11M-nitric acid the order is the more usual Pu(IV) > Np(IV) > U(IV).

Nature of the Nitrate Complexes.—Uranium(IV) in nitrate media at acidities >1M has been shown to yield three spectra: (A) given by the U^{4+} species only; (B) given by UNO_3^{3+}

FIG. 3.   FIG. 4.
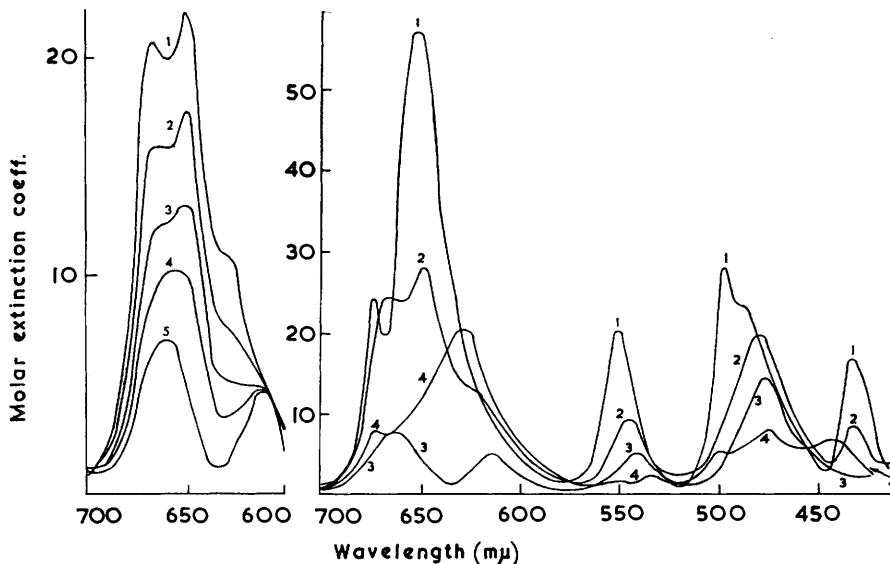
FIG. 3.   Changes in uranium(IV) spectra in 6—14M-nitric acid.
[U(IV)] = 0·35M.   [HNO₃] = (1) 6, (2) 8, (3) 9, (4) 10, (5) 14M.

FIG. 4.   Spectra of different uranium(IV) species.
(1) Spectrum A (U^{4+}).   (2) Spectrum B (UNO_3^{3+}, $U(NO_3)_2^{2+}$ . . ., etc.).   (3) Spectrum C [$H_2U(NO_3)_6$].   (4) UOH^{3+}.
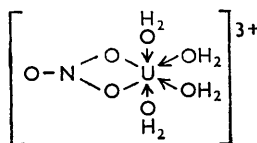
and $U(NO_3)_2^{2+}$; and (C) appearing at [HNO₃] > 4M. These are plotted in Fig. 4, along with that for UOH^{3+}. Spectrum B is also observed in 5—10M-ammonium nitrate containing 1M-nitric acid, and, with only minor changes, for uranium(IV) nitrate solutions in tri-n-butyl phosphate where we should expect the solute to occur principally in the un-ionised form.[5] This makes it probable that at least the third and the fourth complex, $U(NO_3)_3^+$ and $U(NO_3)_4$, also yield spectrum B.

The reflection spectrum of the solid complex, $Cs_2U(NO_3)_6$, is very similar to spectrum C and this implies that the latter can be attributed to a hexanitrato-complex, which might be either the anion $U(NO_3)_6^{2-}$ or the acid $H_2U(NO_3)_6$. Since only traces (<3%) of spectrum C appear in 10M-NH₄NO₃—1M-HNO₃, compared with ~80% in 11M-nitric acid, it is

⁵ Healey and McKay, *Trans. Faraday Soc.*, 1955, **52**, 633.

probable that the acid $H_2U(NO_3)_6$ rather than the anion $U(NO_3)_6^{2-}$ is formed in concentrated nitric acid.

The change in spectrum on addition of the first nitrato-group implies that this group enters the inner co-ordination sphere of the U^{4+} ion. The second, third, etc., nitrato-groups, on the other hand, apparently remain in the outer sphere, forming ion-pairs, -triplets, etc. When ultimately the hexanitrato-species $H_2U(NO_3)_6$ is reached, there is again a change in spectrum, indicating that all the nitrato-groups have gone into the inner sphere; this may be for reasons of symmetry.

It seems possible that the nitrato-group in the first complex is bidentate, a possible configuration being annexed. This would help to explain the difference between the chloro-complex UCl^{3+}, in which the chloride is apparently in the outer sphere, and the nitrato complex UNO_3^{3+}, which is an inner-sphere complex.

EXPERIMENTAL

Preparation of Dicæsium Hexanitratouranate(IV), $Cs_2U(NO_3)_6$.—An ice-cold 0·7M-solution of uranium(IV) nitrate [6] (25 ml.) was slowly added with stirring to a 3M-solution of cæsium nitrate (25 ml.) in concentrated nitric acid. The precipitated complex salt was separated by centrifugation and washed with (i) 8M-nitric acid (20 ml.), (ii) 8M-nitric acid (20 ml.) containing 0·05M-nitrous acid [to destroy traces of hydrazine from the original uranium(IV) preparation], (iii) ice-cold 4M-nitric acid (10 ml.), (iv) ice-cold ethanol (2 × 15 ml.), and (v) ether (2 × 15 ml.). It was then dried for 16 hr. at 10^{-3} mm. The yield was 14·0 g. (90%) [Found: U(IV), 26·8; NO_3, 41·5. Calc. for $Cs_2U(NO_3)_6$: U(IV), 27·2; NO_3, 42·5%]. Analysis of uranium(IV) was by cerimetry with ferrous *o*-phenanthroline as indicator, and nitrate analysis was by distillation as ammonia after reduction with Devarda's alloy. No water was found on infrared examination of the dried salt.

Preparation of Uranium(IV) *Solutions*.—Most of the solutions studied were prepared by dissolving a weighed amount of dicæsium hexanitratouranate(IV) in the appropriate aqueous solution. In most cases the cæsium was completely precipitated as perchlorate; occasionally a small quantity of cæsium remained in solution, but this can hardly have affected the spectra obtained.

When a nitrate-free uranium(IV) perchlorate solution was required, dicæsium hexanitratouranate(IV) (0·5 g.) was dissolved in 0·2M-perchloric acid (10 ml.), and M-sodium hydroxide (5 ml.) was added to precipitate uranium(IV) hydroxide. The latter was separated by centrifugation, washed with 0·01M-sodium hydroxide (2 × 10 ml.), and dissolved in 2M-perchloric acid (25 ml.). All the solutions used were purged with nitrogen. After an hour at 20°, the precipitate had dissolved completely, giving a solution whose spectrum showed no sign of uranium(VI). All the nitrate was accounted for in the combined supernatant liquid and washings.

Spectrophotometry.—The absorption spectra were determined at room temperature (*ca.* 20°) with an Optica CF4 double-beam recording spectrophotometer. For measurements below 400 mμ, the reference solutions were adjusted to the nitrate concentration of the solutions being studied. With the aid of 0·1-cm. silica cells, spectra could be recorded down to 250 mμ.

[6] Streeton and Jenkins, U.K.A.E.A. document AERE-R3938, 1962.