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Abstract

Full Text

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CHEMISTRY

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ON THE PREPARATION AND PROPERTIES OF NITRATE COMPLEX COMPOUNDS OF TETRAVALENT URANIUM

(Presented by Academician V. I. Spitsyn, 22 I 1962)

There are no definite data in the literature on the complex formation of uranium (IV) with NO_3^-. We studied the nitrate complexes of uranium (IV) by spectrophotometric, ion-exchange, and preparative methods. The investigation was carried out in mixed hydrochloric-nitric-acid and hydrochloric-acid–nitric-acid media. To stabilize uranium (IV), small additions of aromatic amines were introduced into the solutions.

The process of complex formation of uranium (IV) with nitrate ions proceeds stepwise. In solutions with nitric acid concentration up to $3N$, predominantly positively charged complex ions UNO_3^{3+}, $U(NO_3)_2^{2+}$, $U(NO_3)_3^{+}$ and molecules $U(NO_3)_4$ are formed. Both these and the others, in color intensity, are considerably inferior to hydrated ions U^{4+}. The maximum difference in molar extinction coefficients is observed at $\lambda = 648$ mμ.

The stability constants of the complexes $U(NO_3)_i^{-i+4}$, where $i = 1 \div 4$, were determined from changes in light absorption at $\lambda = 648$ mμ and from the sorption of uranium (IV) on the cation exchanger KY-2 in the H-form as a function of the concentration of nitric acid. The experimental data were treated by the method of K. B. Yatsimirskii ([1]), somewhat modified as applied to systems containing more than two stepwise-forming complexes. The results of the calculations are given in Table 1.

Table 1

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Ionic strength	Stability constants of complexes	Stability constants of complexes	Stability constants of complexes	Stability constants of complexes	Ionic strength	Stability constants of complexes	Stability constants of complexes	Stability constants of complexes	Stability constants of complexes
Ionic strength	UNO_3^{3+}	$U(NO_3)_2^{2+}$	$U(NO_3)_3^{+}$	$U(NO_3)_4$	Ionic strength	UNO_3^{3+}	$U(NO_3)_2^{2+}$	$U(NO_3)_3^{+}$	$U(NO_3)_4$
2.0	1.58	1.48	0.96	0.35	3.0	1.91	2.02	1.47	0.71
2.5	1.62	1.55	1.06	0.49	3.5	2.29	2.95	2.62	1.51

With increasing ionic strength, the stability of the nitrate complexes of uranium (IV) increases. This feature can be explained by the fact that, as the concentration of salts in the solution increases, the hydration shell of the U^{4+} ions decreases, and thereby interaction with NO_3^- ions is facilitated.

In solutions with nitric acid concentration above $3N$, uranium (IV) forms negatively charged complexes. The charge of the highest anionic complex is -2; i.e., the coordination number of U^{4+} with respect to NO_3^- is 6. The complex ion $[U(NO_3)_6]^{2-}$ is the principal form in which uranium (IV) exists in concentrated nitric acid. With a series of monovalent and divalent cations it forms sparingly soluble hexanitrates. To obtain the latter, a $2 \div 3M$ solution of UCl_4 is diluted 4–10 times (with cooling to approximately 0°C) with concentrated HNO_3 saturated with the nitrate of the corresponding cation. Nitrogen oxides were preliminarily removed from the nitric acid. The precipitated complex nitrates of uranium (IV) were filtered off under vacuum, washed with cold concentrated nitric acid, and dried in air.

We have obtained in pure form the compounds $[U(NO_3)_6]^{2-}$ with the cations of cesium, rubidium, potassium, ammonium, zinc, magnesium, pyridinium, α-aminopyridinium, quinolinium, and α, α'-dipyridylium. The composition of the compounds is expressed, respectively, by the formulas: $Cs_2U(NO_3)_6$, $Rb_2U(NO_3)_6$, $K_3H_3U(NO_3)_{10} \cdot 3H_2O$, $(NH_4)_2U(NO_3)_6$, $ZnU(NO_3)_6 \cdot 8H_2O$, $MgU(NO_3)_6 \cdot 8H_2O$, $(C_5H_5NH)_2U(NO_3)_6$, $(H_2NC_5H_4NH)_2U(NO_3)_6$, $(C_9H_7NH)_2U(NO_3)_6$, and $C_{10}H_8(NH)_2U(NO_3)_6 \cdot 2.5H_2O$. As an example, the results of analysis of samples of uranium(IV) hexanitrates of cesium and ammonium are given below.

$Cs_2U(NO_3)_6$. Found %: Cs 30.37; 30.29; U 27.08; 27.24; NO_3 42.38; 42.61
Calculated %: Cs 30.35; U 27.18; NO_3 42.47

Mol. wt. = 875.93

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$(NH_4)_2U(NO_3)_6$. Found %: NH_4 5.53, 5.74; U 36.93, 36.61; NO_3 57.19; 57.42
Calculated %: NH_4 5.58; U 36.84; NO_3 57.58

Mol. wt. = 646.60

$Cs_2U(NO_3)_6$ and $Rb_2U(NO_3)_6$ crystallize in the form of hexagonal prisms. $K_3H_3U(NO_3)_{10}3H_2O$ and uranium(IV) hexanitrates of ammonium, zinc, and magnesium separate from solution in the form of four-sided prisms of the monoclinic system. $(C_5H_5NH)_2U(NO_3)_6$ is obtained in the form of rhombic crystals. Uranium(IV) hexanitrates of α-aminopyridinium crystallize in the form of tetrahedra. Crystals of $(C_9H_7NH)_2U(NO_3)_6$ are thin triangular plates. Uranium(IV) hexanitrate of α', α'-dipyridylium separates from solution in the form of long needle-shaped crystals. As the size of the crystals decreases, the color of the compounds changes from dark green to greenish-gray.

All complex nitrates of uranium(IV) are readily soluble in water and dilute nitric acid. The dissolution process is accompanied by dissociation of the ions $[U(NO_3)_6]^{2-}$ into NO_3^- ions and lower nitrate complexes of uranium(IV). With increasing concentration of HNO_3, the solubility of the compounds decreases owing to a shift of the equilibrium toward formation of the complex ions $[U(NO_3)_6]^{2-}$. Other conditions being equal, the solubility of the compounds decreases with increasing radius of the outer-sphere cations in the series:

$$Cs^+ < Rb^+ \ll K^+ < NH_4^+; \quad C_9H_7NH^+ \ll H_2NC_5H_4NH^+ < C_5H_5NH^+;$$

$$C_{10}H_8(NH)_2^{2+} \ll Zn^{2+},\ Mg^{2+}.$$

In acetone, methyl and ethyl alcohols, uranium(IV) hexanitrates of ammonium, magnesium, zinc, and all organic cations are readily soluble. Uranium(IV) hexanitrates of rubidium and cesium are practically insoluble. $K_3H_3U(NO_3)_{10} \cdot 3H_2O$ decomposes upon dissolution, with KNO_3 separating in the form of an amorphous precipitate.

In diethyl ether, only uranium(IV) hexanitrates of potassium, magnesium, and zinc dissolve, with decomposition. All the uranium(IV) nitrate complexes isolated by us do not dissolve and do not decompose upon contact with benzene, chloroform, and carbon tetrachloride. On storage in the solid state, uranium(IV) hexanitrates gradually decompose. The decomposition process is due to intramolecular oxidation of uranium by nitrate ions. Oxidation of uranium proceeds nonuniformly throughout the volume. Individual crystals turn yellow, while the bulk of the preparations retains the original color. Apparently, upon oxidation of one of the U^{+4} ions the structure of the crystal lattice is disturbed;

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as a result, the reactivity of neighboring ions increases, and the reaction spreads through the entire crystal at an accelerating rate.

According to stability on storage, the complex nitrates of uranium(IV) are arranged, depending on the outer-sphere cations, in the following series:

$$C_9H_7NH^+ > H_2NC_5H_4NH^+ > Cs^+ > Rb^+ > C_{10}H_8(NH)_2^{2+} > NH_4^+,$$

$$K^+ > Mg^{2+} > C_5H_5NH^+ > Zn^{2+}.$$

In approximately the same sequence, the polarizing power of the listed cations increases. An increase in the polarization of nitrate ions by salt-forming cations leads to a decrease in the strength of the complex $[U(NO_3)_6]^{2-}$ and, at the same time, to an increase in the tendency of uranium to undergo oxidation. The influence of the polarizing power of outer-sphere cations on the properties of compounds in the solid state was noted earlier in works ([2], [3]). Over the course of three months at room temperature, uranium(IV) hexanitrates of quinolinium, α-aminopyridinium and $\alpha\alpha'$-dipyridylium, cesium and rubidium are oxidized by no more than 10%. $ZnU(NO_3)_6 \cdot 8H_2O$ and $(C_5H_5NH)_2U(NO_3)_6$ decompose by 50% within only one to two weeks. In air, $K_3H_3U(NO_3)_{10} \cdot 3H_2O$ rather rapidly loses molecules of water and HNO_3. This circumstance, as well as a number of other factors, prompts one to regard the compound $K_3H_3U(NO_3)_{10} \cdot 3H_2O$ as the crystal hydrate $K_2U(NO_3)_6$, in which part of the water of crystallization is replaced by molecules of HNO_3, KNO_3, and H_2O.

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