

Coordination of technetium anion in uranyl complex with tributylphosphate. Infrared evidence

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A common and a cation-exchange techniques of preparation of tri-n-butylphosphate (TBP) uranyl perrhenato and TBP-uranyl pertechnetato complexes, $\text{UO}_2(\text{XO}_4)_2 \cdot 2\text{TBP}$ ($\text{X} = \text{Re}, \text{Tc}$) are described. The i.r. spectra of these complexes were investigated and discussed from the viewpoint of formation of coordination bond between the ligand (ReO_4^- , TcO_4^-) and the central atom. In the TBP-complexes both the perrhenate and pertechnetate anions exhibit bidentate coordination on the uranyl ion.

Описываются методы приготовления три-н-бутилфосфатных (ТБФ) комплексов перрената и пертехнетата уранила, $\text{UO}_2(\text{XO}_4)_2 \cdot 2\text{TBP}$ ($\text{X} = \text{Re}, \text{Tc}$), обыкновенным и катионно-обменным путем. Были исследованы ИК спектры этих комплексов и обсуждены с точки зрения образования координационной связи между лигандом (ReO_4^- , TcO_4^-) и центральным атомом. В указанных трибутилфосфатных комплексах анионы перрената и пертехнетата проявляются как бидентатно координированные с ионом уранила.

In the presence of actinides the tributylphosphate extraction of pertechnetate anion corresponds to the formation of the mixed complexes of the composition $\text{ML}_{n-1}(\text{TcO}_4) \cdot 2\text{TBP}$ ($\text{M} = \text{UO}_2^{2+}, \text{Th}^{4+}, \text{L} = \text{NO}_3^-, \text{Cl}^-$) [1].

This paper deals with TBP-uranyl pertechnetato- (^{99}Tc), TBP-uranyl perrhenato and TBP-uranyl nitrato complexes to prove the mechanism of coextraction.

Experimental

TBP, purchased from Merck (FRG) was purified by the method of Peppard [2]. NH_4TcO_4 - (^{99}Tc) was product of Radiochemical Centre, Amersham and NH_4ReO_4 of

Schuchardt (FRG). All other reagents were of anal. grade, used without purification.

Concentration of HReO_4 was determined by acidobasic titration. The amount of ^{99}Tc was determined radiometrically using standard of technetium (Amersham). Uranium was estimated by Arsenazo III spectrophotometrically.

The exact volumes of solutions were determined by weighing.

Samples preparation

Uranium trioxide, UO_3 was prepared by annealing of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ at temperature of 390°C for 3 1/2 h [3].

Perrhenate and pertechnetate acids were obtained as follows. Solution of perrhenate or pertechnetate ammonium salt of concentration $0.2\text{--}0.26\text{ mol dm}^{-3}$ was passed through a column of Dowex 50X8 in H^+ form and diluted to 0.1 mol dm^{-3} concentration.

Uranyl perrhenate was prepared by dissolving of stoichiometric amounts of uranium trioxide (0.143 g) in 10 cm^3 of 0.1 mol dm^{-3} HReO_4 . A yellow-green solution was filtered and then evaporated up to crystallization. The crystals were dried at temperature of 200°C [4].

TBP-uranyl nitrate complex, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$: The solution of stoichiometric amounts of uranyl nitrate hexahydrate with TBP in ethanol was evaporated ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.517 g) in ethanol (4 cm^3) with TBP (1.594 g)) and dried in vacuum, resulting in a yellow viscous liquid [5].

TBP-uranyl perrhenate complex, $\text{UO}_2(\text{ReO}_4)_2 \cdot 2\text{TBP}$: To uranyl perrhenate (0.1315 g) in ethanol the stoichiometric amount 0.89 cm^3 of TBP solution in ethanol (0.1001 g TBP/cm^3) was added and ethanol evaporated. The complex was observed as a yellow viscous liquid (U: calculated: 18.27%, found: 17.8%).

Uranyl pertechnetate, $\text{UO}_2(\text{TcO}_4)_2 \cdot 1.5\text{H}_2\text{O}$: Instead of classical method of preparation from UO_3 and HTcO_4 , which needs the use of relatively high pertechnetate acid concentration [6] we used cation-exchange reaction between $\text{TcO}_4^-/\text{NH}_4^+$ and UO_2^{2+} bound on cation exchanger column. Further advantage is that the reaction between uranium and pertechnetate proceeds without a strict control of $\text{UO}_2^{2+}:\text{TcO}_4^-$ ratio during the preparation and the product is not contaminated by free acid.

A column with cation-exchange resin (Dowex 50X8 in H^+ form) was saturated with uranyl passing through $0.2\text{ M-UO}_2(\text{NO}_3)_2$ and washed by water to neutral reaction of eluate. Then 0.1 M-HTcO_4 (10 cm^3) was passed and the yellow-green eluate was evaporated in air and dried at temperature of 80°C [6], yielding yellow crystals. (U: calculated: 38.21%, found: 37.6%; Tc: calculated: 31.78%, found: 31.3%).

TBP-uranyl pertechnetate complex, $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{TBP}$: 8.0 cm^3 of the solution of uranyl pertechnetate in ethanol ($6.012\text{ mg }^{99}\text{Tc/cm}^3$) were added to 2.59 cm^3 of TBP solution in ethanol (0.1001 g TBP/cm^3) and ethanol was evaporated at room temperature up to a constant weight of residue. The complex represented a fluorescent yellow viscous liquid (U: calculated: 21.09%, found: 21.5%; Tc: calculated: 17.54%, found: 18.1%).

Infrared measurement

The infrared spectra in the range 500—4000 cm^{-1} were recorded with Perkin—Elmer (USA), Model 567 and IR-75 (Zeiss, Jena) infrared spectrometers.

Results and discussion

The infrared spectra of TBP-uranyl pertechnetate (Fig. 1) have been compared with those of uranyl pertechnetate, TBP-uranyl perrhenate, and TBP-uranyl nitrate complexes, the last being known from literature [7—11].

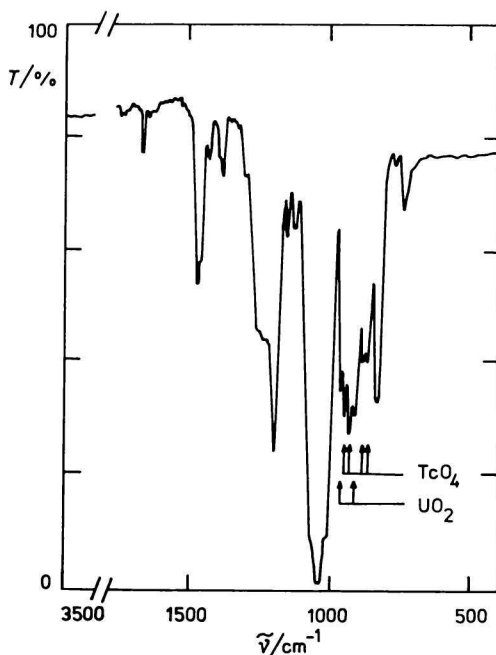


Fig. 1. Infrared spectrum of uranyl pertechnetate complex with tributylphosphate, $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{TBP}$.

In Table 1 are summarized the principal vibrational frequencies of the complexes under study.

The spectrum of uranyl perrhenate has many absorption bands in the 960—850 cm^{-1} region which belong to the vibrational frequencies of ReO_4^- as well as UO_2^{2+} ions. Bands at 900 and 955 cm^{-1} are ν_s and ν_{as} stretching frequencies of uranyl ion. Complementary absorption bands at 855, 895, 910, and 930 cm^{-1} belong to ReO_4^- ion according to the decreased symmetry by coordination of ReO_4^- to uranyl ion. In the i.r. spectrum of uranyl perrhenate there is no singlet of

Table 1

IR spectra $\tilde{\nu}$ (cm^{-1}) of monohydrate of uranyl perrhenate and of TBP-uranyl perrhenato and TBP-uranyl pertechnetato complexes

Type of vibration	$\text{UO}_2(\text{ReO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{UO}_2(\text{ReO}_4)_2 \cdot 2\text{TBP}$	$\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{TBP}$
$\nu(\text{UO}_2^{2+})$	955, 900	950, 900	950, 900
$\nu(\text{O}_2\text{ReO}_2) (\text{C}_{2v})$	930, 910 895, 855	935, 915 890, 880	—
$\nu(\text{O}_2\text{TcO}_2) (\text{C}_{2v})$	—	—	935, 915 890, 855
$\nu(\text{P}=\text{O})$	—	1190	1190
$\nu(\text{P}-\text{O}-\text{C})$	—	1030	1030
$\nu(\text{O}-\text{H})$	3460, 3320	—	—
Lattice water			
$\delta(\text{H}-\text{O}-\text{H})$	1600	—	—
Coordinated water	590	—	—

symmetric noncoordinated ReO_4^- ion at 918 cm^{-1} [12]. On the basis of four fundamental frequencies observed in the spectrum it can be assumed that there are bidentately coordinated groups O_2ReO_2 (symmetry C_{2v}). In low frequency region appears a relatively sharp peak for coordinated water [13].

The i.r. spectrum of TBP-uranyl perrhenato complex is generally devoided of any absorption attributable to the presence of coordinated or lattice water ($\nu(\text{OH})$, $\delta(\text{H}-\text{O}-\text{H})$). A shift of $\text{P}=\text{O}$ stretching frequency from 1280 cm^{-1} (for TBP) to 1190 cm^{-1} (for the complex) is produced by coordination between TBP and uranyl ion. Absorption band at 1030 cm^{-1} belongs to $\text{P}-\text{O}-\text{C}$ (butyl) bond [7, 14] and there is no change observed in comparison between the $\text{UO}_2(\text{ReO}_4)_2 \cdot 2\text{TBP}$ and free TBP.

Absorption bands of stretching frequency of $\text{P}=\text{O}$ and $\text{P}-\text{O}-\text{C}$ bonds of TBP-uranyl pertechnetato complex are the same as for TBP-uranyl perrhenato complex. Six vibrational frequencies in the $850-950 \text{ cm}^{-1}$ region are for UO_2^{2+} and TcO_4^- ions. A shift of ν_{as} of UO_2^{2+} ion from 955 (for $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{H}_2\text{O}$) [15] to 950 cm^{-1} is observed. Four fundamental frequencies for TcO_4^- (symmetry C_{2v}) in the TBP-uranyl pertechnetato complex (Fig. 1) give evidence of bidentate coordination of TcO_4^- on the uranyl ion. Hence, coordination number of uranium in the complex $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{TBP}$ equals 8. It is supposed that in the mixed complex, $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)_2 \cdot 2\text{TBP}$, which should be formed in the course of solvent extraction at excess of nitrate anions [1], the coordination number of uranyl ion will be the same as for the complex $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{TBP}$ because NO_3 group in TBP-uranyl nitrato complex is also bidentately coordinated on uranyl ion [8, 9]. Asymmetric stretching frequency of UO_2^{2+} ion is at 950 cm^{-1} in the TBP-uranyl

pertechnetato complex and at 940—945 cm^{-1} in the TBP-uranyl nitrate complex [10, 11] and it is supposed that in the mixed complex it will be between these values. Four fundamental frequencies of TcO_4 group at 950—850 cm^{-1} will not interfere with neighbours. The stretching frequencies of NO_3 groups in $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{A}$ complexes [11], except ν_2 frequency of coordinated ONO_2 , are not within the region of P—O—C(butyl) frequencies, too. Thus, i.r. spectroscopy offers further possibility of obtaining the coextracted technetium in tributylphosphate extracts of uranium.

Further, the bidentate coordination of TcO_4^- to the uranyl ion confirms that the coextraction mechanism, proposed for trace amounts of technetium [1, 16]



should proceed via the inner-sphere ligand exchange and not due to a simple ion-pairing between UO_2NO_3^+ and TcO_4^- , as supposed later [17]. This new type of coextraction should be strongly dependent on the nature of central atom as it was demonstrated in our previous paper concerning exchange in the systems with uranyl and thorium [1].

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