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Solvent-extraction Complex of Uranium(VI) with *cis*, *syn*, *cis*-Dicyclohexano-18-crown-6

WEN-JI WANG*, BOZHONG CHEN
Department of Nuclear Science, Fundan University, Shanghai, China
PEIJU ZHENG, BOYI WANG and MING WANG
Center of Measurement and Analysis, Fundan University, Shanghai, China

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Abstract

The extraction of U(VI) with dicyclohexano-18-crown-6 (mixed isomers or isomer A) from HCl medium is effective and selective, and can be used for separating and analysing uranium and thorium. However, little is known of the properties of the extraction complex of uranium with crown-ether in organic phase. In this paper we report the preparation, characteristic and structure of the crystalline extraction complex **Ia**–UO_2Cl_2–HCl–H_2O, **Ia** being isomer A of dicyclohexano-18-crown-6.

After extracting uranium(VI) from aqueous hydrochloric acid solution with **Ia** in 1,2-dichloroethane, the crystalline product of the extraction complex was prepared from the organic phase by diluting with a non-polar solvent at 25 °C. The content of uranium, crown-ether and HCl was determined. The IR spectrum of the crystals shows that the strong hydronium–crown ether/oxygen hydrogen bond absorption is found in the region 2300–2400 cm^{-1}. The chemical shift in the range 9–12 ppm was observed. The ^{1}H NMR signal of hydronium protons appears at 9.890 ppm. The results of assay correspond to the formula $(\mathbf{Ia})_2 \cdot (H_3O^+)_2 \cdot UO_2Cl_4{}^{2-}$.

Crystal structure of the extraction complex has been determined by X-ray crystallography. Crystals are monoclinic, space group $C_{2/c}$ (No. 15) $a = 32.464$, $b = 10.203$, $c = 21.616$ Å, $\beta = 119.73°$ and $Z = 4$. In the complex each of the two H_3O^+ cations is anchored in the crown-ether cavity by three stronger hydrogen bonds (distances approximately 2.65 Å), whereas uranium forms $UO_2Cl_4{}^{2-}$ with Cl^- as counterion about 8 Å away from the H_3O^+.

After comparing the extractability of a series of crown-ethers, it is concluded that dicyclohexano-18-crown-6 is best for extracting tetra- and hexavalent uranium from HNO_3 and HCl media [1, 2, 3, 4]. The extraction of the uranyl ion with dicyclohexano-18-crown-6 (mixed isomers or isomer A) in 1,2-dichloroethane from aqueous hydrochloric acid solution is effective and selective, and can be taken in separating and analysing uranium and thorium [5]. However, little is known of the properties of extraction complexes of uranium with crown-ether in an organic phase. There is an interesting question of why dicyclohexano-18-crown-6 has high extractability for uranium in aqueous hydrochloric acid solution, even though the cavity size of crown-ether does not match the ionic size of uranium(VI). Hence, the preparation, composition and crystal structure of the crystalline complex **Ia**–UO_2Cl_2–HCl–H_2O have been investigated, **Ia** being dicyclohexano-18-crown-6 isomer A (*i.e. cis*, *syn*, *cis*-dicyclohexano-18-crown-6).

The crystalline extraction complex was prepared by the following procedures: dicyclohexano-18-crown-6 (m.p. 48–56 °C) was a Fluka AG product. Isomer A was separated from mixed isomers and purified using the procedure of Izatt *et al.* [6]. Purity was checked by infrared spectrometry [5]. The extraction of uranium(VI) from 4N HCl–0.025 M UO_2Cl_2 aqueous solution with an equal volume of 0.1 M **Ia** in 1,2-dichloroethane was carried out at 25 °C. In order to get the crystalline complex after phase separation, the organic phase was diluted slowly by a double volume of benzene, and stood overnight for the single crystal growth.

According to the method which was described in ref. 5, assay of the crystalline complex in question is as follows: (*w*/*w*%) dicyclohexano-18-crown-6 isomer A. *Anal.* Calc.: **Ia**, 62.32; H^+, 0.168; $UO_2{}^{2+}$, 22.62; Cl^-, 11.88. Found: **Ia**, 63.46; H^+, 0.150; $UO_2{}^{2+}$, 21.75; Cl^-, 11.90%. Which corresponds to the formula $(\mathbf{Ia})_2 \cdot UO_2Cl_2 \cdot 2HCl \cdot xH_2O$.

IR spectra of the complex were recorded with an IFS-113 V infrared spectrometer, and showed that

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*Author to whom correspondence should be addressed.

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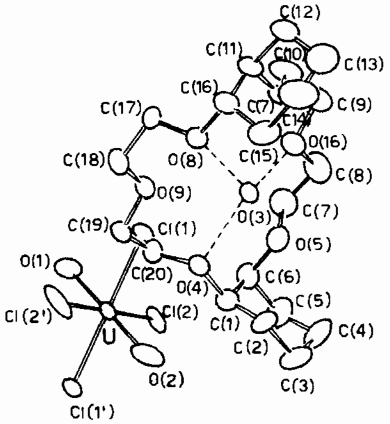

Fig. 1. Projection of a portion of the $(\mathbf{Ia})_2 \cdot (H_3O^+)_2 \cdot UO_2Cl_4^{2-}$ structure. The uranium atom is on the axis of 2 symmetry. O(3) is the oxygen atom of hydronium ion, which is located between crown-ether and uranium.

the strong hydronium–crown ether/oxygen hydrogen bond absorption is found in the region 2300–2400 cm^{-1}.

Structure analysis of the title complex has been carried out. All intensity data were collected on the Enraf-Nonius CAD4 diffractometer with Mo Kα radiation. The SDP programs were used in solving structure. The position parameters of uranium were solved by Patterson and direct methods. All other non-hydrogen atoms were found on a subsequent difference-Fourier synthesis. All positions and isotropic or anisotropic thermal parameters were refined by full-matrix least-squares procedure to R factor of 0.045. Crystal data: $(C_{20}H_{36}O_6)_2(H_3O^+)_2UO_2Cl_4^{2-}$, $M = 1198.82$, yellow crystal, monoclinic, space group $C_{2/c}$ (No. 15), $a = 32.464$, $b = 10.203$, $c = 21.616$ Å, $\beta = 119.73°$ and $Z = 4$.

The three-dimensional structure of the complex is shown in Fig. 1. The uranium atom is on the axis of 2 symmetry, and is surrounded by two oxygen atoms and four chloric ions as anion $UO_2Cl_4^{2-}$ which forms a distortional tetragonal bipyramid, about 8 Å away from the hydronium ion. In the complex each of the two H_3O^+ cations is anchored in the crown-ether cavity by three strong hydrogen bonds (O(4,6,8)...O(3) distances of 2.644, 2.627 and 2.694 Å. O(4,6,8) are ether oxygen atoms and O(3) is the oxygen atoms of hydronium ion). This bonding is analogous to that found in a complex of a tetracarboxylic 18-crown-6 ether with H_3OCl [7]. From the crystal structure analysis it can be seen that in the unit cell the uranium as counterion $UO_2Cl_4^{2-}$ is sandwiched between two H_3O^+-complexes of crown-ether. As mentioned above, it is reasonable that the process of extraction of uranium(VI) from aqueous hydrochloric acid solution with dicyclohexano-18-crown-6 isomer A (**Ia**) in 1,2-dichloroethane can be written as

$$UO_2^{2+} + 2\mathbf{Ia} + 2H_3O^+ + 4Cl^- = (\mathbf{Ia})_2 \cdot (H_3O^+)_2 \cdot UO_2Cl_4^{2-}$$

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