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Abstract

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STRUCTURE OF POLYNUCLEAR DICHARGED URANIUM-OXYGEN COMPLEXES AND THEIR ARRANGEMENT IN THE STRUCTURE OF AN AQUEOUS SOLUTION

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In dilute aqueous solutions of uranyl salts, which are 2–1-electrolytes, uranyl UO_2^{2+} has coordination number 6 and is located in the channels of the water structure along the channel axis ([1]). Hydrolysis leads to the formation in solution of polynuclear complexes ([2–7]); the most reliable data may be considered to be those on the existence of the ions $U_2O_5^{2+}$ and $U_3O_8^{2+}$. Let us suppose that 2 (or 3) uranyl ions, each of which is surrounded by 6 molecules of water, are situated in 2 (or 3) adjacent channels of one layer of the water structure (Figs. 1a and 2a). It is precisely in this case that hydrolysis reactions can proceed:

$$2UO_2^{2+} + H_2O \rightleftarrows U_2O_5^{2+} + 2H^+,$$

$$3UO_2^{2+} + 2H_2O \rightleftarrows U_3O_8^{2+} + 4H^+.$$

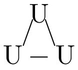
The charge of uranyl is concentrated in the uranium atom, while the oxygen atoms are almost electroneutral ([8]); therefore, the U—O—U bond will be formed in the equatorial plane common to the reacting uranyls. Since complex ions exist as independent constituents, the U—O bond in them must be strong, with a considerable degree of covalency. Of great importance for elucidating the structure of these complexes is also the fact that they are formed not only during hydrolysis, but also when uranium trioxide is dissolved in solutions of uranyl salts ([2]). In both cases the color of the solution changes from yellow-green, characteristic of aqueous solutions in which uranyl is present, to orange, characteristic of uranium trioxide; this indicates the appearance in the aqueous solution of constituents in which there is a uranyl bond characteristic of uranium trioxide (the U—O distance is of the order of 2.0 Å) ([9,10]). From the foregoing, we consider that $U_2O_5^{2+}$ and $U_3O_8^{2+}$ in solution have the structure shown by us in Figs. 1b and 2b. The linear uranyl ions are arranged perpendicular to the linear chain U—O—U—O ..., located in one layer of the water structure; the distances U—O_I in the individual uranyls and in the U—O ... chain are of the same order. In the complexes there are pres–

Fig. 1. Formation of the ion $U_2O_5^{2+}$:
a –two uranyls in adjacent channels of the water structure;
b –the ion $U_2O_5^{2+}$, formed from 2 uranyls bound to one another by an O^{2-} ion. The O_I—U—O_I axis of uranyl is perpendicular to the plane of the drawing, which coincides with the equatorial plane of the uranyls: one oxygen atom O_I is located behind the plane of the drawing, the other in front of it; the projection of the oxygen atoms onto the plane of the drawing is indicated by dotted lines; water molecules are indicated by thin solid lines; the outlines of the complex in the equatorial plane are indicated by a thick solid line.

are elements of the same chain with uranyl bonding that is present in UO_3, but the essential difference is that in $U_2O_5^{2+}$ and in $U_3O_8^{2+}$ there is both a chain with uranyl bonding and separate UO_2^{2+} ions,

Fig. 2. Formation of the $U_3O_8^{2+}$ ion: *a*–3 uranyls in neighboring channels of the water structure; *b*–the $U_3O_8^{2+}$ ion formed from 3 neighboring uranyls, linked to one another into a straight chain by O^{2-} ions. The designations are the same as in Fig. 1.

i.e., the uranyl bond will be in two mutually perpendicular directions. The nonlinear structure of the polynuclear complex $U_3O_8^{2+}$ with formation of the triangle



in the common equatorial plane of the uranyls seems to us unlikely, since each uranium atom would then have to give, in the equatorial plane, two asymmetrically arranged bonds. The complexes under consideration also cannot have the structure of a chain $[O_I - U - O_I] - O - [O_I - U - O_I] - \cdots$, since uranyl, because of the electroneutrality of its oxygens, does not give strong axial bonds.

Fig. 3. Formation of the $U_2O_7^{2-}$ ion: 2 uranyls, located in neighboring channels of the water structure, are linked into a straight chain by an O^{2-} ion; at both ends of the chain there are also O^{2-} ions. The designations are the same as in Fig. 1.

Around a uranyl that has become part of a complex ion, 6 water molecules can no longer be accommodated, owing to steric factors; however, each uranyl in the equatorial plane will be surrounded by water molecules in the manner most closely approximating the environment of 1 uranyl ion in solution. The $U_2O_5^{2+}$ ion will be surrounded in the equatorial plane by 8 water molecules, and the

$U_3O_8^{2+}$ ion by 12 molecules, as is evident from Figs. 1b and 2b, drawn to scale. The coordination number of the terminal uranyls in polynuclear complexes decreases to 5; for the middle one it is 6 (in the equatorial plane, 4 water molecules and 2 oxygen atoms). The number of water molecules around a complex containing n uranium atoms is equal to $4n$.

The general formula for the composition of doubly charged positive uranium-oxygen complexes, constructed according to the principle of a linear chain of uranyls located in neighboring channels of the water structure and linked by oxygen atoms, may be represented as follows:

$$[U_nO_{3n-1}]^{2+}. \qquad (1)$$

The formula may be given a form showing that the complexes are built from uranyls:

$$[n\,UO_2^{2+} \cdot (n-1)\,O^{2-}]^{2+}. \qquad (2)$$

In these formulas n is the number of uranium atoms or the number of uranyl ions. Both according to formula (1) and according to formula (2), at $n = 1$ we have uranyl, UO_2^{2+}; at

for $n = 2$, $U_2O_5^{2+}$ is obtained; for $n = 3$, $U_3O_8^{2+}$ is obtained. The next ion will have the form $U_4O_{11}^{2+}$; it is possible that in some very small amount it is also present in solution, but at larger n the complexes have not been detected experimentally in solution. Arland, Hietanen, and Sillén (^{6}) proposed, for polynuclear uranyl complexes in solution, the formulas $UO_2 \cdot [(OH)_2UO_2]_n^{2+}$ and $UO_2(OUO_2)_n^{2+}$, obtained in the mathematical treatment of data on the hydrolysis of the uranyl ion. Arland et al. resolve the question of the structure of polynuclear uranyl complexes by analogy with the structure of the crystals $BaUO_2O_2$, $CaUO_2O_2$, $UO_2(OH)_2$, without taking into account the structure of water and of aqueous solutions containing uranium. They suppose that, as n increases, the polynuclear uranyl complexes in aqueous solution form a flat layer in which UO_2—$4O$ or UO_2—$6OH$ coordination is realized. The view set forth above by us of the linear structure of $U_2O_5^{2+}$ and $U_3O_8^{2+}$, with UO_2—$2O, 4H_2O$ coordination for the uranyls situated in the middle of the chain and UO_2—$O, 4H_2O$ coordination for the uranyls situated at the ends of the chain, differs from the view of the cited authors on the structure of the complexes, since, first, our view proceeds from the experimentally found coordination number of uranium in aqueous solution and from the placement of uranyl ions in the channels of the water structure (^{1}), and, second, from the presence in the uranyl complexes of a U—O... chain with uranyl bonding, characteristic of UO_3. The composition of the positive polynuclear complexes can be described both by our formulas (1) and (2) and by the second formula of Arland et al.; the first formula of these authors is not consistent with ours.

With increasing pH of solutions of uranium salts, not positive but negative polynuclear uranium-oxygen complexes are formed in solution. Let us consider the following experimentally established compounds: uranate, Na_2UO_4, diuranate, $Na_2U_2O_7$, tetrauranate, CaU_4O_{13} (^{7}), heptauranate, $Na_2U_7O_{22}$ (^{11}), and octauranate, $Na_2U_8O_{25}$ (^{12}). In all these cases complex anions are present. On the basis, first, of the fact that the presence of UO_2^{2+} in uranates has been established roentgenographically (^{13,14}), and, second, of the fact that formation of negative polynuclear complexes is only the next stage after formation in solution of positive polynuclear complexes (^{11}), we consider that the polynuclear uranium-oxygen anions should be regarded as uranyl-oxygen complexes. The uranyl groups are arranged in the channels of the water structure in such a way that their equatorial planes coincide, and the uranium and oxygen atoms in this plane are situated on one straight line, forming the same chain with uranyl bond O—U—O ..., which was observed in the positive complexes; but at the ends of the chain in the negative complexes there are oxygen atoms (Fig. 3), whereby the negative polynuclear complexes differ from the positive complexes, in which uranium atoms are situated at the ends of the chain.

For polynuclear uranium-oxygen complexes carrying charge (−2), the following general formula may be proposed:

$$[U_nO_{3n+1}]^{2-}.$$

For $n = 1$ there arises UO_4^{2-}; for $n = 2$, $U_2O_7^{2-}$; for $n = 4$, $U_4O_{13}^{2-}$; for $n = 7$, $U_7O_{22}^{2-}$; for $n = 8$, $U_8O_{25}^{2-}$. It is not excluded that, depending on pH, there may also be other polynuclear complexes in solution, for example at $n = 3$, the complex $U_3O_{10}^{2-}$. As in the case of the positive complexes, the general formula expressing the composition of the negative polynuclear complexes can be given another form, which will emphasize the presence of uranyl:

$$[n\,UO_2^{2+} \cdot (n+1)O^{2-}]^{2-}.$$

If one compares the formulas of the positive and negative complexes, one cannot fail to see their very close similarity, since they reflect a fundamentally identical structure of divalent cations and anions (a rectilinear chain of uranyls linked by oxygen atoms); the difference in the structure of these complexes is reduced to the fact that in the negative complexes oxygen atoms stand at the ends of the chain, whereas in the positive complexes uranium atoms do.

Hexavalent uranium is capable of forming various uranium-oxygen configurations with uranyl bonds in mutually perpendicular directions. When the uranyl bond is present in one direction, linear configurations are formed (the uranyl ion; a chain with uranyl bonding in α-UO_3). The polynuclear complexes considered here provide examples of more complex uranium-oxygen configurations, when the uranyl bond is present in two mutually perpendicular directions. We regard the cubic modification of UO_3 ([15]) and $UO_2(OH)_2$ ([16]) as compounds in which uranyl bonding is observed in three mutually perpendicular directions in space.

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Note: Figure translations are in progress. See original paper for figures.