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Abstract

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Owing to the great similarity of the physical and chemical properties of hydrated and anhydrous uranates, when considering the structure of hydrated uranates it is necessary to take into account the results of investigations of the crystal structure of anhydrous uranates ([1–9]). However, recently works have appeared ([10,11]) in which the structure of hydrated uranates is interpreted without taking these data into account.

In all structures of monouranates there is a uranyl grouping UO_2 with a U—O distance close to 1.9 Å. In contrast to the majority of uranyl salts (see, for example, ([12])), in uranates the oxygen of the uranyl grouping is bonded not only to uranium atoms but also to other cations, and therefore the U—O bond length in the case of uranates is appreciably greater (by 0.15—0.20 Å) than in uranyl salts. For this reason one cannot agree with the assertion ([10]) that the value 1.9 Å is most characteristic for uranyl. The secondary bonds ($U—O_{II}$) are essentially ionic (the bond strength is less than unity). The chain structure of polynuclear complexes proposed in ([10]) is based on the idea of the possibility of formation of several mutually perpendicular covalent U—O bonds. As an example of a compound with such bonds, to some extent one may consider cubic uranium trioxide (the only U(VI) compound in which the strength of all bonds is the same and equal to unity). However, the structure of this oxide is not specific to uranium and occurs in some other trioxides. We believe that the ideas ([10]) about discrete polynuclear uranate ions do not agree with the structures of hydrated uranates, which contain infinite uranyl-oxygen motifs.

Complex fluorides in which there are more than two fluorine ions per uranyl ion differ in their structure from uranates because of the possibility of forming discrete ions, for example $[UO_2F_4]^{2-}$. The corresponding complexes containing no other addends except water and hydroxide are unknown. Therefore, consideration of uranates as hydroxo-aqua complexes ([11]), analogous to fluoride complexes, is not consistent with all the experimental data on the structure of uranates and does not permit an approach to understanding their properties.

The X-ray investigation carried out by us of hydrated and some anhydrous uranates confirms the structural similarity between both groups of uranates. Most monouranates are characterized by the presence of one of three infinite

uranyl-oxygen motifs of composition $(UO_2)O_2$ ([5]). A change in the coordination number of the cations (in connection with the increase of their radius) causes either a change in the type of the $(UO_2)O_2$ motif, or a distortion of the symmetry of the layer. In the case of polymorphic varieties, during the $\alpha \rightarrow \beta$ transition, as a rule, an increase is observed in the volume per formula unit (V/Z). The $\alpha \rightarrow \beta$ transformation (900°) in potassium monouranate corresponds to the transition of an ordered structure into a disordered one.

However, uranates are known in which it is impossible to identify a uranyl-oxygen motif. Thus, the cubic modification of $PbUO_4$ may be regarded as an example of a structure with uranyl groupings statistically arranged parallel to one of the four possible directions in space (along the threefold axes). β-K_2UO_4 is built according to the principle of closest cubic cation-anion packing, with the uranium atoms located in octahedral voids. In this case the uranyl grouping may be statistically arranged along one of three directions in space. The potassium mesouranate of composition K_4UO_5 and the mixed uranate $Na_{0.75}Ca_{0.25}UO_{3.625}$, which we have investigated, have an analogous structure.

Alkali-element diuranates are characterized by a defective structure of the $CaUO_4$ type, with hexagonal layers of composition $(UO_2)O_{1.5}$. Among other anhydrous alkali-element polyuranates, we have studied the structure of potassium trihexauranates. This is a phase of variable composition with a homogeneity range from $K_2O \cdot 3UO_3$ to $K_2O \cdot 6UO_3$. In the structure of this phase an infinite hexagonal uranyl-oxygen layer $(UO_2)O_2$ can also be distinguished, but the layers are situated exactly one above another, unlike the mono- and diuranates of the alkali elements. Some of the uranium atoms are situated between the layers, apparently also in the form of uranyl ions, the oxygen atoms of the uranyl grouping (or some of them) probably simultaneously entering into the composition of the principal uranyl-oxygen motif.

The polyuranates of certain divalent elements that we have studied have a somewhat different character. Their behavior toward acids and a number of other chemical properties are analogous to those observed in the case of alkali uranates. At the same time, investigation of the crystal structure of these compounds shows that they are more correctly regarded as double oxides or substitutional solid solutions.

The double oxides structurally close to α-UO_3 and to the hexagonal modification of U_3O_8 include ZnU_3O_{10} and MgU_3O_{10}. Cadmium tri- and pentauranate, which has a homogeneity range from $CdO \cdot 3UO_3$ to $CdO \cdot 5UO_3$, is structurally close to rhombic uranium suboxide-oxide. The phase $SrO \cdot 1.5\text{-}1.75\,UO_3$ found in the case of strontium has a distorted structure of the CaF_2 type, probably with an ordered arrangement of Sr and U. Analogous phases have been found in the $BaO–UO_3$ system. These phases are structurally close to UO_2. Thus, in polyuranates there are present either uranyl groupings (alkali-element polyuranates) or the corresponding chains
–O–U–O–U–O–.

The similarity of the structures of hydrated and anhydrous uranates may be judged on the basis of data on the phase composition of precipitated sodium uranates ([13]), on the structure of uranyl hydroxides ([14,15]), hydrated barium and lead polyuranates ([16,17]), and also our investigations of the structure of precipitated sodium and potassium uranates.

In anhydrous uranates, uranium has coordination numbers 6 and 8, and in monouranates octahedra $(UO_2)O_4$ occur much more often than cubes $(UO_2)O_6$. This is apparently due in part to the more considerable compression of oxygen in the latter case (the O–O distance is of the order of 2.5 Å). Conversely, in hydrated uranates, hydroxides, and basic uranyl salts, coordination of oxygen, hydroxyl, and water is almost exclusively along the vertices of a cube (compressed along an axis of order 3). This is evidently caused by a decrease in the O–O distance due to the formation of hydrogen bonds. Coordination number 6 has been found only in β-$UO_2(OH)_2$. Therefore the basic structural element of hydrated uranates is hexagonal or pseudohexagonal layers, analogous to those found, for example, in $CaUO_4$.

The oxygen atoms in uranates (apart from the oxygen of the uranyl grouping) may be replaced by F^-, OH^-, and H_2O without substantial change of the structure. In this case the charge of the layer $UO_2X_2 (X = O, F, OH, H_2O)$ decreases according to the degree of substitution, and consequently the total charge of the ions situated between the layers also decreases. In the case of complete substitution of ato-

oxygen atoms with fluorine, the structure UO_2F_2 is obtained; upon replacement of half the oxygen, $NaUO_3F$. In solid solutions $NaUO_3F$—$Na_2U_2O_7$, fluorine replaces an even smaller amount of oxygen.

Complete replacement of oxygen by hydroxyl ions leads to the formation of uranyl hydroxide (the cation sites may be occupied by water molecules), while partial replacement leads to aqueous uranates. Replacement of part of the hydroxyl ions by water molecules is accompanied by the formation of basic uranyl salts. In this case, both ordered and disordered arrangements of oxygen and hydroxyl in the layer, as well as of cations and water between the layers, are possible, i.e., the formation of berthollide and daltonide phases (in the latter case, superstructure lines will be observed on the X-ray patterns).

Sodium uranates obtained at high pH values had the composition $Na_2O \cdot 2.3\,UO_3$ and the $CaUO_4$ structure. The unit-cell parameters of $Na_2O \cdot 2.3\,UO_3$ ($a = 3.97$; $c = 17.66$)* are close to the parameters of the fluorouranate $NaUO_3F$ ($a = 3.96$; $c = 17.70$). Upon partial replacement of sodium ions by larger water molecules, the charge of the uranyl–oxygen layer decreases, and the distance between the layers increases ($a = 4.01$; $c = 18.11$). The phase with the $CaUO_4$ structure can exist up to the composition $Na_2O \cdot 4UO_3$. The structure of the next phase, corresponding to more acidic uranates with the ratio $Na_2O : UO_3 < 1 : 4$, is characterized by a less compact stacking of layers than in the $CaUO_4$-type structure (each succeeding layer lies exactly above the preceding one). This

structure is close to the structures of natural barium and lead uranates and to the structure of anhydrous potassium trihexauranate (in contrast to the latter, in aqueous polyuranates all uranium is part of the uranyl-oxygen layer). This phase is characterized by the presence of a subcell $a \sim 7$, $b \sim 4$, and $c \sim 7$. The precipitated potassium triuranate has the same structure (more precisely, uranates close in composition to the triuranate). The indicated structure can be stable only when large cations (Ba, Pb, K) and water molecules are located between the layers.

The homogeneity region of aqueous sodium uranates with $Na_2O : UO_3 < 1 : 4$ includes uranyl hydroxide and the sparingly soluble basic nitrate. We found that precipitation of the basic nitrate is already observed upon addition of one mole of NaOH to $UO_2(NO_3)_2$ (in 1 M solutions). If $UO_2(NO_3)_2$ and UO_3 are taken with the aim of obtaining a 1 M solution of $UO_2(OH)NO_3$, complete dissolution of UO_3 likewise does not occur, and a precipitate of the basic nitrate is formed. Both precipitates give identical X-ray patterns, the brightest lines of which are indexed with the parameters of the above-mentioned subcell ($a \sim 7$, $b \sim 4$, and $c \sim 7$). Thus, the structures of aqueous uranates, uranyl hydroxide, and basic nitrates are of the same type and are characterized by the presence of hexagonal (or pseudohexagonal) uranyl-oxygen layers, in which oxygen can be replaced by hydroxyl and water.

The arrangement of water molecules around the uranyl ion in aqueous polyuranates is the same as in aqueous uranyl solutions ([10]) and in solid uranyl nitrate ([18]). This allows us to consider the processes occurring during titration of uranyl salts with alkali as replacement of water molecules in the hydrate shell of the uranyl ion by hydroxyl ions and then by oxygen, according to the scheme:

$$\underset{\text{uranyl ion}}{[UO_2(H_2O)_6]^{2+}} \rightarrow \underset{\text{polynuclear complex ion}}{[(H_2O)_4UO_2(OH)_2UO_2(H_2O)_4]^{2+}} \rightarrow$$

$$\underset{\substack{\text{solid basic}\\ \text{nitrates}}}{[UO_2(OH,H_2O)_2]_n^{n+}} \rightarrow \underset{\substack{\text{uranyl}\\ \text{hydroxide}}}{[UO_2(OH)_2]_\infty^0} \rightarrow \underset{\substack{\text{aqueous}\\ \text{uranates}}}{[UO_2(O,OH)_2]_n^{n-}}$$

From the moment the precipitate of the basic salt or uranyl hydroxide separates, replacement of addends proceeds in the solid phase and the processes slow sharply; as a result, a continuous change in the charge of the layer is possible. The forming

* Parameter values are given throughout in kiloxes.

compounds may have a wide range of homogeneity; therefore the composition of hydrous polyuranates usually does not correspond to simple stoichiometric formulas.

Thus, from the point of view of their structure in the solid state, uranates may be divided into two groups: 1) true uranates, in which,

in one form or another, the corresponding structural units are present, the composition of which depends on the composition of the uranate ($Me^{II}UO_6$, $Me^{II}(UO_2)O_2$, $Me^{I}_2(UO_2)O_2$, $Me^{I}(UO_2)O_{1.5}$, $Me^{II}_xUO_2(O,OH)_2$, etc.); 2) anhydrous polyuranates of divalent elements, which are more correctly regarded as double oxides or solid solutions.

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