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Abstract

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E. S. MAKAROV

HOMOLOGOUS SERIES OF URANIUM OXIDES $U_{nO_{2n+2}}$

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The development of inorganic chemistry over the last 5-7 years has been characterized by the discovery of homologous regularities in the chemical composition of a number of oxides of transition elements. These interesting regularities were previously known only in organic chemistry. For inorganic chemistry they were first found by the Swedish crystal chemist Magnéli and co-workers in the study of the oxides of tungsten, molybdenum, vanadium, and titanium ($^{1-8}$).

Thus it turned out that the composition of the oxides of tungsten and molybdenum obeys the homologous formulas $M_{nO_{3n-1}}$ and $M_{nO_{3n-2}}$, while the oxides of titanium and vanadium obey the formulas $M_{nO_{2n-1}}$ (where M is a metal, n is an integer). For example, for titanium oxides, all homologues of the series $\mathrm{Ti}_{nO_{2n-1}}$ from $n = 1$ to $n = 10$ have been synthesized, isolated in individual form, and characterized by X-ray methods, i.e., the oxides: TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15}, Ti_9O_{17}, $\mathrm{Ti}_{10}O_{19}$.

Many investigators in various countries of the world have studied the chemistry of uranium oxides (see (^{10})). The chemistry of the uranium-oxygen system is extremely complicated owing to the formation of oxides of variable composition, as well as so-called "nonstoichiometric" oxides, i.e., those which do not satisfy a simple stoichiometric ratio of uranium and oxygen, for example: U_3O_7, U_3O_8, U_4O_9, U_5O_{12}, etc.

On the basis of the proposition concerning the duality of the chemical nature of uranium (^{9}), which, depending on the valence it exhibits, resembles now the lanthanides and now the elements IV A, V A, VI A, it could be assumed that the compositions of uranium oxides also obey some general homologous regularity. Indeed, this supposition is apparently confirmed by all available data on the composition and structure of uranium oxides, as will be shown below.

In Fig. 1, on the composition axis UO_x, vertical strokes mark the compositions of uranium oxides obeying the general formula $\mathrm{U}_{nO_{2n+2}}$ (where n is an integer); it turns out that all eight initial homologues of this series actually exist in the form of oxides established in the experimental investigations cited below. In Fig. 1 these oxides are marked by the corresponding formulas above the ordinates of the compositions.

Fig. 1. Homologous series of uranium oxides $U_{nO_{2n+2}}$.

Figure 1: Fig. 1. Homologous series of uranium oxides $U_{nO_{2n+2}}$.

$n = 1$. UO_4^{2-}. Uranium tetroxide has not been isolated in the free state, but it exists in the form of the uranate ion UO_4^{2-}, and also in the form of hydrates; for example, the dihydrate $UO_4 \cdot 2H_2O$ is well known (^{10}).

$n = 2$. $U_2O_6 = UO_3$. Uranium trioxide is the usual form of the highest oxidation state of uranium, long ago and firmly established by numerous authors. At least five polymorphic modifications of UO_3 are known (^{11}).

Recently we confirmed Zachariasen' s data (^{12}) on the structure of hexagonal oxide α-UO_3, obtained in our laboratory by L. M. Kuznetsov by thermal decomposition of the trihydrate of tetravalent oxalate uranium, $U(C_2O_4)_2 \cdot 3H_2O$. In exactly the same way, by neutron diffraction we confirmed the cubic structure of the ReO_3 type for δ-UO_3, first found by E. Wait (^{13}). In addition, we synthesized two other oxides of composition UO_3, whose structure has not yet been determined.

$n = 3$. U_3O_8. The so-called uranous-uranic oxide, most frequently encountered in chemical practice, is known in two polymorphic varieties. The low-temperature modification U_3O_8 is stable up to $\sim 400°$ and has a rhombic structure with lattice constants $a = 11.91$; $b = 6.71$; $c = 8.27$ kX, occurring also in the form of two monoclinically distorted varieties with the same parameters and angles of 89 and 91°, respectively (^{14}). Above 400°, U_3O_8 has a trigonal structure with constants $a = 6.801$; $c = 4.128$ kX (^{15}). It is possible that both modifications of U_3O_8 are oxides of variable composition, with an oxygen deficiency. Despite many attempts, the arrangement of the atoms in both modifications cannot be considered definitively established.

Fig. 1. Homologous series of uranium oxides $U_{nO_{2n+2}}$.

$n = 4$. $U_4O_{10} = U_2O_5$. This uranium oxide has been found in many investigations, and recently it has been regarded by Rundle, Baenziger, Wilson, and McDonald (^{16}) as the low-oxygen boundary of a homogeneous region, possibly existing within the limits $UO_{2.5}$—UO_3. According to other data (^{17}), this region exists within the limits $UO_{2.56}$—$UO_{2.66}$ (U_3O_8). In view of the fact that the equilibrium phase diagram of the uranium–oxygen system has not at present been established, the exact temperature and concentration limits of stability of the oxide U_2O_5, as, indeed, of other uranium oxides as well, remain for the time being unknown. The most reliable crystallochemical data on U_2O_5 were reported by Rundle et al. (^{16}), who succeeded in obtaining a single crystal of this oxide and establishing that it belongs to the rhombic system, with cell dimensions: $a = 8.27$; $b = 31.65$; $c = 6.72$ Å; the arrangement of the atoms has not been determined.

$n = 5$. U_5O_{12}. Grønvold and Haraldsen ([17]), as well as Perio ([18]), in studying the products of low-temperature oxidation of uranium dioxide, found a tetragonal oxide close to the composition $UO_{2.40}$, which corresponds to the formula U_5O_{12}. The lattice constants, according to Perio: $a = 5.364$; $c = 5.531$ Å; $c/a = 1.031$. The arrangement of the atoms has not been established.

$n = 6$. $U_6O_{14} = U_3O_7$. The first indication of the existence of this oxide was given by P. Jolibois ([19]). Subsequently, in the study of the low-temperature oxidation of uranium dioxide, the existence of the oxide $UO_{2.33} = U_3O_7$ was confirmed by a number of investigators ([17,18,20]). The structure of this oxide is

tetragonal and, according to P. Perio (18), has: $a = 5.436$; $c = 5.389$ Å; $c/a = 0.991$. D. S. Anderson, for another crystal setting, gives $c/a = 1.016$. The arrangement of atoms in U_3O_7 has not been established.

$n = 7$. U_7O_{16}. This compound apparently belongs to the third tetragonal uranium oxide with the axial ratio $c/a = 1.010$, which Perio (18) discovered together with the two preceding ones ($UO_{2.40}$ and $UO_{2.33}$). Its theoretical composition $UO_{2.285} = U_7O_{16}$ corresponds well to Perio' s (18) proposed experimental range $UO_{2.28-2.31}$, which he was unable to refine.

$n = 8$. $U_8O_{18} = U_4O_9$. The existence of this oxide has been firmly established by many investigations, among which we shall mention the recent works of Hoekstra and Siegel (21), Hering and Perio (22), and Belbeoch, Piekarski, and Perio (23). Until recently it was accepted that $U_4O_9 = UO_{2.25}$ corresponds to the upper limit of oxygen saturation of the phase of variable composition based on cubic uranium dioxide, $UO_{2.00-2.25}$ (10). At the same time, according to numerous X-ray powder investigations, it was found that the constant of the cubic lattice, as the degree of oxidation increases, gradually decreases from $a = 5.47$ Å for UO_2 to $a = 5.43$ Å for $UO_{2.25}$ (approximate values).

However, recently Perio (23) succeeded in synthesizing a single crystal of U_4O_9, whose X-ray investigation confirmed cubic syngony but gave an unexpectedly large value of the lattice constant, quadrupled along the edge, $a = 4 \cdot 5.433 = 21.73$ Å. This fact indicates the discreteness of the chemical composition of the oxide U_4O_9. The arrangement of atoms in U_4O_9 cannot be considered definitively established.

For the time being, these data limit further advance toward larger values of n in the homologous series U_nO_{2n+2}. Analysis of this formula and Fig. 1 show that an increase in n rapidly leads to vanishingly small differences in the chemical composition of neighboring oxides, as a result of which the investigator enters first a difficult, and then a completely impassable, experimental "forest" of an innumerable multitude of discrete uranium oxides tending in their composition toward UO_2, but never exactly reaching it.

Apparently, this circumstance explains the widely known fact that in practice the experimenter never has an oxide of ideal composition UO_2, but always has somewhat more oxidized samples UO_x, where x is slightly greater than two, for example $UO_{2.008}$, $UO_{2.010}$ (18).

One may nevertheless hope that such oxides as U_9O_{20}, $U_{10}O_{22} = U_5O_{11}$, $U_{11}O_{24}$, and others will soon be established experimentally.

The poor knowledge of the details of the crystal structure does not at present make it possible to connect the homology of the chemical composition of uranium oxides with the arrangement of atoms in them. Such a connection undoubtedly must exist, and the efforts of crystal chemists should be directed toward revealing this connection and toward the search for the "molecules" U_nO_{2n+2}, without which the chemical essence of homology would in this case be unclear.

Let us also note that the establishment of homology in the composition of inorganic compounds opens an entirely new path for interpreting the chemical nature of berthollides analogous to oxides of variable composition $UO_{2.0-2.25}$. In the light of the homologous regularity, such berthollides cannot be regarded, as has been done up to the present, as "phases of variable composition," as a "continuous set of compounds." The new data compel us to change these views and to consider composition ranges such as $UO_{2.2-2.25}$ as a discontinuous, discrete set of individual chemical species united by a common homologous regularity and having very similar chemical compositions, crystal structures, and properties.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadsky
Academy of Sciences of the USSR

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References

1. A. Magneli, Acta Crystallogr., **6**, 495 (1953).
2. B. Blomberg, L. Kihlborg, A. Magneli, Arkiv Kemi, **6**, 133 (1953).
3. G. Andersson, Acta Chem. Scand., **8**, 1599 (1954).
4. A. Magneli, B. Blomberg-Hansson et al., Acta Chem. Scand., **9**, 1382 (1955).
5. S. Andersson, A. Magneli, Naturwiss., **43**, 495 (1956).
6. S. Andersson, B. Collen et al., Acta Chem. Scand., **11**, 1641 (1957).
7. S. Andersson, XVI Congrès International de Chimie Pure et Appliquée, Paris, 1957.

8. S. Andersson, A. Sundholm, A. Magnéli, Acta Chem. Scand., **13**, 989 (1959).

9. E. S. Makarov, *Crystallochemistry of simple compounds of uranium, thorium, plutonium and neptunium*, Publishing House of the Academy of Sciences of the USSR, 1958.

10. G. T. Seaborg, J. J. Katz, *Chemistry of the Actinide Elements*, Moscow, 1960.

11. G. Hoekstra, S. Siegel, *Uranium–oxygen system: the region from* U_3O_8 *to* UO_3, Report No. 1548 at the Second Geneva Conference on the Peaceful Uses of Atomic Energy, 1958.

12. W. H. Zachariasen, Acta Crystallogr., **1**, No. 5, 265 (1948).

13. E. Wait, J. Inorg. and Nucl. Chem., **1**, No. 4/5, 309 (1955).

14. B. Khodura, Ya. Maly, *On the structure of* U_3O_8. II International Conference of the UN on the Peaceful Uses of Atomic Energy, A/Conf. 15/P/2099, Czechoslovakia, 20 June, 1958, 1958.

15. S. Siegel, Acta Crystallogr., **8**, No. 10, 617 (1955).

16. R. E. Rundle, N. C. Baenziger et al., J. Am. Chem. Soc., **70**, 99 (1948).

17. F. Gronvold, H. Haraldsen, Nature, **162**, No. 4106, 69 (1948).

18. P. Perio, Bull. Soc. chim. France, 1953, 256, 840.

19. P. Jolibois, C. R., **224**, 1395 (1947).

20. J. S. Anderson, Bull. Soc. chim. France, 1953, 781.

21. G. Hoekstra, S. Siegel, Report No. 737 at the I Geneva Conference on the Peaceful Uses of Atomic Energy, 1955.

22. H. Hering, P. Perio, Bull. Soc. chim. France, 1952, No. 3/4, 351.

23. B. Belboch, C. Piekarski, P. Perio, Bull. Soc. franc. mineral. et cristallogr., **83**, No. 7/9, 206 (1960).

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