AN X-RAY DIFFRACTION STUDY OF THE DEHYDRATION OF 12-SILICOTUNGSTIC AND 12-PHOSPHOMOLYBDIC ACIDS

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Structural studies of the dehydration products of 12-phosphotungstic acid of initial composition H₃PW₁₂O₄₀·29H₂O have shown that the 12-phosphotungstate anion of composition (PW₁₂·O₄₀)⁻³ does not change its structure up to complete dehydration of the initial crystals; in the crystal lattice the 12-phosphotungstate anions are closely packed in all products of drying, starting with the 23 hydrate; dehydration is reversible, the hydration occurring with a change in the crystal lattice [1]. The structure and properties of the highly hydrated forms of the other 12-heteropoly acids are very similar to the structure and properties of the corresponding hydrates of 12-phosphotungstic acid [2]. In this connection it was of interest to study the structures of the dehydration products of 12-silicotungstic and 12-phosphomolybdic acids.

The initial products were the highly hydrated hydrates: H₄SiW₁₂O₄₀·29H₂O and H₅PW₁₂O₄₀·29H₂O. The atomic-molecular structure of these hydrates is known [2]. An x-ray study of the initial hydrates confirmed that we actually had hydrates with 29 water molecules for one 12-heteropoly anion. The arrangement of anions of the composition AMₑ₊₂O₄₀ (A = P, Si; Me = W, Mo) in the crystal lattice is similar to the arrangement of carbon atoms in the diamond crystal lattice. In a unit cell a = 23.2 Å there are eight molecules of acid. The arrangement of water molecules in the unit cell of these hydrates was studied in [3]. The water molecules are outside the anions and form clusters of 29 molecules in which the molecules are arranged in groups: 1 + 4 + 6 + 12 + 6. The central molecule of the cluster is surrounded by groups of water molecules forming a tetrahedron, octahedron, dodecahedron and further — again an octahedron. There are eight of these clusters in the unit cell and they are arranged like the atoms in a diamond. The crystal lattice of highly hydrated hydrates of 12-heteropoly acids can therefore be considered as diamond-type lattices inserted into one another, one of them being formed by the AMₑ₊₂O₄₀ anions and the other by clusters of 29 water molecules.

EXPERIMENTAL

Dehydration of 12-silicotungstic acid. Crystals of the composition H₄SiW₁₂O₄₀·29H₂O were dehydrated in vacuum at 20°. The specimens in the form of a powder were first weighed and placed in a vacuum desicator, dehydrated in it for a certain period and then weighed again. Figure 1 shows the dehydration of 12-silicotungstic acid to the composition H₄SiW₁₂O₄₀·11H₂O. For comparison purposes, Fig. 1 gives the dehydration curves of 12-phosphotungstic acid. The form of these curves is the same for both acids. It was noted in [1] that for "stable" hydrates, the composition of which corresponds to a plateau on the dehydration curve, the presence of a cubic body-centered lattice is characteristic. Thus, for 12-phosphotungstic acid a cubic body-centered lattice with a = 12, 13 Å was detected for 23-11-*, and 5- hydrates. The 11-hydrate of 12-silicotungstic acid also has a body-centered cubic lattice with a = 12, 14 Å. For a hydrate with 23 water molecules this type of lattice was not detected, despite the fact that there is a plateau on the dehydration curve for this composition. The diffraction pattern from this hydrate has a strong background; the diffraction lines are very wide and therefore difficult to measure. The reason for the difference of the structure H₄SiW₁₂O₄₀·29H₂O from the structure H₅PW₁₂O₄₀·23H₂O can readily be explained if we compare the width of the plateau for compositions with 23 water molecules on the corresponding dehydration curves. The width of the plateau for H₅PW₁₂O₄₀·23H₂O is 7-10 min, and for H₄SiW₁₂O₄₀·23H₂O it is only about 2 min. In such a short time the (SiW₁₂O₄₀)⁻⁴ anions are evidently unable to occupy positions corresponding to a body-centered cubic lattice. The unbalance of the lattice of the hydrate H₅SiW₁₂O₄₀·23H₂O is also shown by the form of the diffraction pattern. The hydrate H₄SiW₁₂O₄₀·5H₂O was obtained on heating 12-silicotungstic acid in air at 100°. The crystal lattice of this hydrate, like the lattice of the pentahydrate of 12-phosphotungstic acid, is cubic body-centered with a = 12, 13 Å. As a result of the dehydration of 12-silicotungstic acid for compositions corresponding to a fairly wide plateau on the dehydration curve, "stable" hydrates are therefore formed with a body-centered cubic lattice (a = 12, 13 Å).
Fig. 1. Dehydration curves of 12-silicotungstic (a) and 12-phosphomolybdic (b) acids.

The agreement of the structure of "stable" hydrates of 12-silicotungstic acid with the structure of the corresponding hydrates of 12-phosphotungstic acid points to the constancy of the structure of 12-silicotungstate anion (SiW\(_{12}O_{40}\))\(^{7-}\) during dehydration to the composition H\(_4\)SiW\(_{12}O_{40}\)*5H\(_2\)O. Since the unit cell parameter of "stable" hydrates of 12-silicotungstic acid does not change with change in the water content, the (SiW\(_{12}O_{40}\))\(^{7-}\) anions in the lattice are closely packed. This has enabled us to find the crystallochemical radius of the anions (SiW\(_{12}O_{40}\))\(^{7-}\); this is 5.2 Å, which agrees well with the crystallochemical radius of the anion (PW\(_{12}O_{40}\))\(^{3-}\) [1]. When 12-silicotungstic acid is heated in air at 220-250°, when 4-5 water molecules are still retained, the lattice of the pentrahydrate made up of (SiW\(_{12}O_{40}\))\(^{7-}\) anions is not disrupted. We should mention the strong hygroscopicity of 12-silicotungstic acid. In contrast to 12-phosphotungstic acid the 11-hydrates of 12-silicotungstic acid when kept in air for 18 h collect water up to compositions with 20-23 water molecules. The structure of hydrates of 12-silicotungstic acid whose compositions differ from "stable" compositions could not be interpreted. We can simply mention that the loss of almost each water molecule leads to a change in the form of the diffraction pattern.

The heating of 12-silicotungstic acid to 400° causes breakdown of the 12-silicotungstate anions. The diffraction patterns from products formed at temperatures of 400, 500, 600 and 700° are perfectly identical, i.e., their structures are the same. A similar structure was also found previously for the product obtained by roasting 12-phosphotungstic acid at 700° [4]. This structure, found at room temperature, is similar to that of the high-temperature tetragonal tungsten trioxide. The appearance of a tetragonal lat-