Crystal Structure of the β-12-Tungstosilicate Anion

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Summary Crystals of β-$K_4SiW_{12}O_{40}$,$9H_2O$ have been shown by *X*-ray diffraction to contain a $SiW_{12}O_{40}^{4-}$ anion which is a geometrical isomer of the Keggin structure.

IT is known that 12-tungstosilicic acid has two isomers, the α and β (or normal and iso) forms, which have an unknown structural relationship.[1]

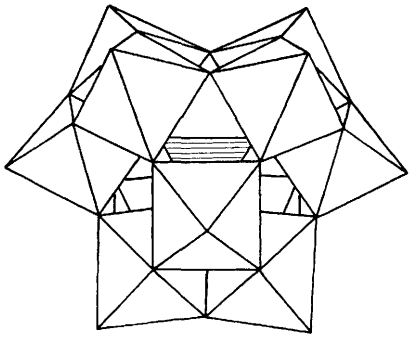

FIGURE 1. Model of the Keggin structure. The octahedra and shaded tetrahedron represent WO_6 and SiO_4, respectively.

Ordinarily, the β-isomer is formed in low yield together with the main product, the α-form, from a mixed solution of sodium tungstate, sodium silicate, and strong acid. Recently

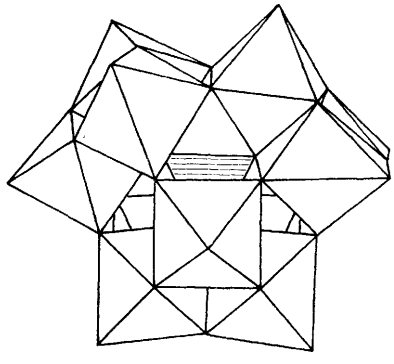

FIGURE 2. Model of the β-$SiW_{12}O_{40}^{4-}$ anion

Souchay *et al.* reported that addition of acid to sodium tungstate solution prior to mixing with sodium silicate gives very pure β-12-tungstosilicic acid.[2]

Three-dimensional *X*-ray structure determination of α-$Ba_2SiW_{12}O_{40}$,$16H_2O$ crystals has shown that this α-isomer has the well known Keggin structure (see Figure 1)[3] The present communication reports the structure of β-$SiW_{12}O_{40}^{4-}$ which is a geometrical isomer.

The potassium salt of β-12-tungstosilicic acid prepared by Souchay's method was found to be stable in air. The samples are yellow-white crystals of rectangular plate form. *Crystal data*: $K_4SiW_{12}O_{40}$, $9H_2O$, orthorhombic, $a = 20{\cdot}617(3)$, $b = 15{\cdot}567(4)$, $c = 12{\cdot}953(2)$ Å, $U = 4156{\cdot}56$ Å^3, $Z = 4$, space group P_{nma}. The intensities of 2007 independent reflections were collected on a Rigaku automatic four-circle diffractometer (Mo-K_α radiation with graphite monochromator).

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares technique to an *R* value of 0·147 without absorption corrections. The temperature factors of oxygen atoms were assumed to be isotropic but the other atoms were anisotropic. The water molecules have not yet been located and further refinement is continuing.

The model of the β-isomer built with WO_6 octahedra shown in Figure 2 can be obtained by 60° rotation of one of the trigonal W_3O_{13} units of the Keggin model around its threefold axis. This model corresponds to one of the five possible structures suggested by Baker and Figgis for isomers of Keggin type polyanions.[4]

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