Crystal Structure of α-$P_2W_{18}O_{62}^{6-}$ Anion

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Summary Crystals of α-$Ba_3P_2W_{18}O_{62}\cdot 29H_2O$ have been shown by *X*-ray diffraction to contain the α-$P_2W_{18}O_{62}^{6-}$ anion, which is a geometrical isomer of β-$P_2W_{18}O_{62}^{6-}$ solved by Dawson in 1953.

18-TUNGSTO-2-PHOSPHORIC acid and its salts always have two isomers, the α- and β-forms.[1,2] The two-dimensional *X*-ray structure determination of β-$K_6P_2W_{18}O_{62}\cdot 14H_2O$ by Dawson[3] showed that the β- form of the polyanion has the

structure shown in Figure 1, but the origin of the isomerism was not known. We report the structure of the α- form in crystals of the barium salt.

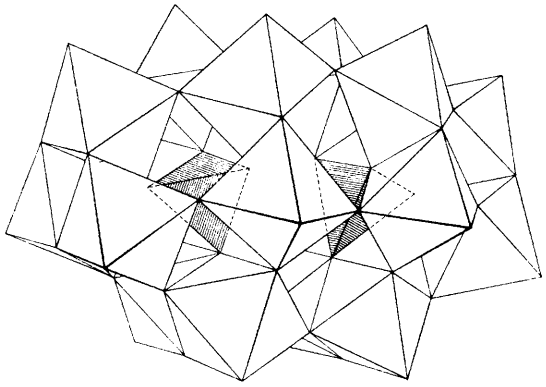

FIGURE 1. β-$P_2W_{18}O_{62}^{6-}$ anion.

Lemon-yellow rhombic crystals (0·1 × 0·1 × 0·07 mm) of α-$Ba_3P_2W_{18}O_{62}$·29 H_2O, which were stable in air, were precipitated from a solution prepared by cation-exchange from the ammonium salt synthesized by Wu's method.[1] *Crystal data:* $Ba_3P_2W_{18}O_{62}$·29H_2O, orthorhombic, space group $Pmn2_1$; a = 20·18(3), b = 14·94(2), c = 12·98(2) Å; U = 3913·3 Å^3; D_m = 4·49, D_c = 4·50 g cm^{-3}; Z = 2. The intensities of 3130 independent reflections up to 2θ = 60° were collected on a Rigaku automatic four-circle diffractometer with Mo–K_α radiation and a graphite monochromator.

The structure was solved by the heavy-atom method. Refinement by block-diagonal least-squares using anisotropic temperature factors for tungsten, barium, and phosphorus and isotropic ones for oxygen atoms reduced the R-value to 16·9% at the present stage. Water molecules have not yet been located.

The polyhedral models of the β- and α-$P_2W_{18}O_{62}^{6-}$, shown in Figures 1 and 2, can be divided into two PW_9O_{34} units which are made from the well known Keggin structure[4] of $PW_{12}O_{40}^{3-}$ by removing a W_3O_{15} ring formed from three WO_6 octahedra by sharing corners. A similar structure was recently found in the 9-molybdophosphate, $H_6PMo_9O_{34}^{3-}$.[5]

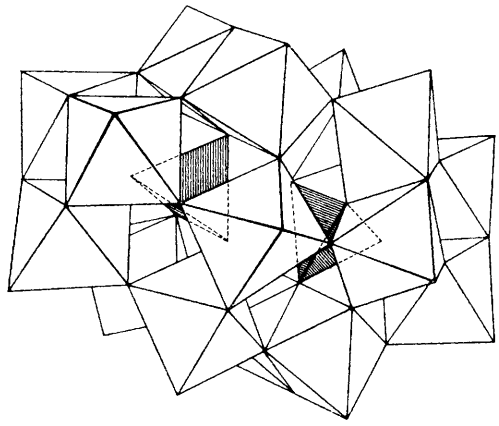

FIGURE 2. α-$P_2W_{18}O_{62}^{6-}$ anion.

The two half-units can be joined at 6 oxygen atoms in two different ways to yield α- and β-$P_2W_{18}O_{62}^{6-}$ anions. In the β-form the anion has a mirror plane passing through these six points, whereas in the α-form the two units are combined in a staggered arrangement as shown in Figure 2 and the polyanion has D_{3d} symmetry, since the mirror plane in the β-model of D_{3h} symmetry is lost.

The present model is included in the six models proposed by Baker and Figgis[6] as possible isomeric structures of the 18-heteropolyacid.

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