X-Ray Crystal Structure of a New Heteropolyanion, $[P_4W_8O_{40}]^{12-}$, with an X:M Ratio of 1:2

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Summary The structure of the first heteropolyanion, $[P_4W_8O_{40}]^{12-}$, with an X:M ratio of 1:2, has been determined from single crystal *X*-ray studies of the sodium salt; the idealized anion has $\bar{4}2m$ symmetry and consists of a shell of WO_6 octahedra and PO_4 tetrahedra made up of four PW_2O_{13} groups linked by corner sharing and a sodium atom is situated in the centre of the polyanion.

THE complexity of the heteropolyanions is such that structural studies are necessary to characterize the species involved. The first structural reports on heteropolyanions with an X:M ratio[1] of 1:3 appeared recently for the 1:3 arsenomolybdate polyanions $[As_2Mo_6O_{26}]^{6-}$ and $[(PhAs)_2Mo_6O_{24}]^{4-}$,[2] $[(PhAs)_4Mo_{12}O_{46}]^{4-}$,[3] $[(CH_3As)_2Mo_6O_{24}]^{4-}$,[4] and $[H_4As_4Mo_{12}O_{50}]^{4-}$ [5] using ^{17}O n.m.r. studies (in solution), and *X*-ray studies in the last two cases. We report here the structure of the first heteropolyanion, $[P_4W_8O_{40}]^{12-}$, with an X:M ratio of 1:2.

During an attempt to prepare $Na_3PW_3O_{13}$ following the method of Kehrmann and Mellet,[6] colourless prismatic crystals of the sodium salt of the title polyanion were obtained. A small crystal (0·05 mm^3) was selected and unit-cell and intensity data were collected using a Philips PW 1100 diffractometer with graphite monochromated Mo-K_α radiation (λ = 0·7107 Å).

Crystal data: $Na_{12}O_{40}P_4W_8$(aq.), monoclinic, a = 19·610(8); b = 18·339(6); c = 16·173(8) Å; β = 94·80(3)°; U = 5796 Å^3; D_m (flotation in CH_2I_2–CCl_4) 3·29(3) g cm^{-3}, space group $I2/a$ or Ia [equivalent to $C2/c$ (C_{2h}^6, No. 15) or Cc (C_s^4, No. 9), respectively] from absences. The centric space group was chosen on the basis of the *E*-statistics and this choice was borne out by subsequent smooth refinement.

The tungsten positions were calculated from the Patterson map and further atoms were located from difference Fourier syntheses. The anion seems to be $[P_4W_8O_{40}]^{12-}$, although some of the anion oxygens may be water molecules (a feature not uncommon in heteropoly-type anions) thus reducing the rather large charge on the anion. Using anisotropic temperature factors on the tungsten atoms, and a $1/\sigma^2$ weighting scheme, the refinement gives wR = 0·13† for the anion group alone. When likely sodium and water positions are included, refinement gives a current wR = 0·095 for 2280 independent reflections with $I \geq 3\sigma(I)$.

The structure consists of layers of the anion unit in the y–z plane centred at $x = \frac{1}{4}$ and $\frac{3}{4}$. Each of these layers may be considered to contain zig-zag strings of the anion unit generated by the centres of symmetry at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{3}{4}$) for the $x = \frac{1}{4}$ sheet, and the centres at ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{4}$) and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) for the $x = \frac{3}{4}$ sheet. The distance between these sheets (anion oxygen to anion oxygen) is *ca.* 3·9 Å, and this mode of packing helps to explain the observation that the crystals have a cleavage plane perpendicular to the long axis of the crystal.

† $wR = \Sigma w^{\frac{1}{2}}(|F_o - F_c|)/\Sigma w^{\frac{1}{2}}(|F_o|)$.

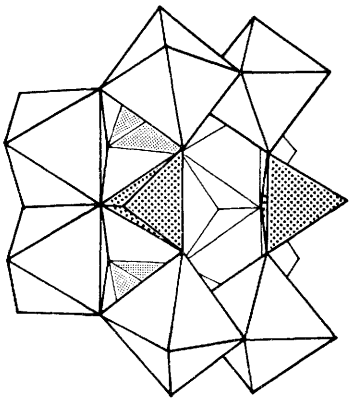

FIGURE. The idealized structure of $[P_4W_8O_{40}]^{12-}$.

The novel structure of the polyanion is shown in the Figure. It consists of a shell of WO_6 octahedra and PO_4 tetrahedra made up of four PW_2O_{13} groups linked by corner sharing, closely resembling the 'shell' of the Keggin anion[7] which consists of four M_3O_{13} groups linked by corner sharing. In both anions, the octahedra within the groups are edge shared. The idealized $[P_4W_8O_{40}]^{12-}$ polyanion has $\bar{4}2m$ symmetry and is clearly of the same structural type as the $[H_4As_4Mo_{12}O_{50}]^{4-}$ polyanion, but in a lower M : X series. Both anions have a large hole in the centre which is too large to accommodate a Keggin type central atom, *i.e.*, in the Keggin $X^{n+}M_{12}O_{40}^{(8-n)-}$ anions; the X_t–O distances are typically in the range 1·6—1·9 Å, whereas the radii of the cavities in the P_4W_8 and the As_4Mo_{12} anions are *ca.* 2·6 and *ca.* 2·8 Å, respectively.

One remarkable feature of the $[P_4W_8O_{40}]^{12-}$ anion is the presence of a sodium atom in the centre on the two-fold axis, so the anion could be written as $[NaP_4W_8O_{40}]^{11-}$. This cage-type inclusion of sodium has also been observed for $(NH_4)_{17}Na(NaW_{21}Sb_9O_{83}).14H_2O$,[8] in which the sodium to oxygen distance is 2·44(5) Å [2·68(9) Å in the present work] and the sodium co-ordinations are 6 and 12, respectively. At the present stage of refinement, the octahedra appear to be highly distorted and the averaged tungsten–oxygen distances W–O_a, W–O_b, W–O_c, and W–O_d are 1·71, 1·91, 2·12, and 2·25(7) Å, respectively, where O_a and O_b are bound to one and two tungsten atoms only and O_c and O_d are bound to one phosphorus atom as well as one and two tungsten atoms, respectively. Dehydration studies and the density measurement indicate the formula $Na_{12}[P_4W_8O_{40}]\cdot(20 \pm 2)H_2O$; however, if the anion charge is reduced by replacing anion oxygens with OH^- or OH_2 groups, then some of the lattice water molecules would have to be OH^- in order to balance the $12Na^+$ per ion.‡ Further refinement is in progress and full details will be published elsewhere.

(*Received*, 21*st June* 1977; *Com.* 616.)

‡ We are grateful to a referee for drawing our attention to this possibility.

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