18-Tungstotetracobalto(II)diphosphate and Related Anions: a Novel Structural Class of Heteropolyanions

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Summary The $P_2Co_4(H_2O)_2W_{18}O_{68}^{10-}$ anion contains four edge-linked $Co^{II}O_6$ octahedra with coplanar cobalt atoms, in addition to two fragments of the Keggin structure.

The 11-tungstocobalto(II)phosphate ion,[1,2] $PCo(H_2O)W_{11}O_{39}^{5-}$, slowly reacts with Co^{2+} in aqueous solution at pH 7—7·5 to give a new heteropolyanion of empirical formula $PCo_2W_9O_{34+n}H_{2n}^{5-}$. The latter is more conveniently obtained by the prolonged reaction at 90—100° of an aqueous mixture of composition $H^+ : HPO_4^{2-} : Co^{2+} : WO_4^{2-} = 11:2:4:18$ and is separated and purified as the K^+ salt. An analogous red-violet tungstocobaltoarsenate is similarly prepared, as are anions containing bivalent manganese (brown-yellow), nickel (yellow), copper (green), and zinc (white). The *d–d* spectra show that near-octahedral $Z^{II}O_6$ groups are present (Z = Co, Ni, Cu). The potassium salts of the cobalt complexes and of the tungstozincoarsenate give virtually identical *X*-ray powder diffraction patterns. The anions are acid-sensitive, giving first $XZ(H_2O)W_{11}O_{39}^{5-}$ and then $XW_{12}O_{40}^{3-}$ below about pH4 (X = P, As; Z = Co, *etc.*). These and other reactions, and the natures of the ternary heteropolyanion by-products formed during the preparation, are being studied.[3]

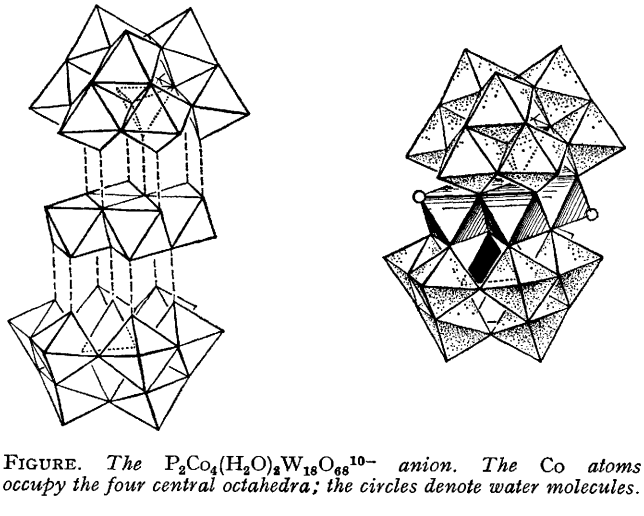

Figure. *The* $P_2Co_4(H_2O)_2W_{18}O_{68}^{10-}$ *anion. The* Co *atoms occupy the four central octahedra; the circles denote water molecules.*

The results of a single-crystal study of what has proved to be $K_{10}[P_2Co_4(H_2O)_2W_{18}O_{68}],20H_2O$ are of immediate interest. *Crystal data:* monoclinic, space group $P2_1/n$; a = 15·808(2), b = 21·353(3), c = 12·324(2) Å, β = 92·23(1)°; D_m = 4·38(2), D_c = 4·379 g cm^{-3}, Z = 4 (empirical formulae). Intensity data were collected (Picker automatic diffractometer, Mo-K_α radiation) for 5414 independent reflections with $2\theta > 45°$. The structure was solved using data from 1693 reflections with $2\theta > 30°$. Using a routine procedure—Lorentz and polarization (no absorption) corrections, Wilson scaling, normalization (to get E values), and symbolic addition—a group of 150 large amplitudes was found, yielding a sharpened electron density map (E map) in which all heavy atoms were clearly apparent. Successive F_{obs} Fourier maps revealed all remaining non-hydrogen atoms. Least-squares refinement with the curtailed data set has converged to an R index of 0·073, and is being continued with the full data set.

The main features of the $P_2Co_4(H_2O)_2W_{18}O_{68}^{10-}$ anion (point symmetry C_{2h}-$2/m$), the largest and most massive heteropolyanion ($M = 4729$) of known structure, are already clear and are shown in the Figure. A flat central set of four edge-linked CoO_6 octahedra, resembling a fragment of a composite layer in $Co(OH)_2$, separates two fragments of the well-known Keggin[4] ($PW_{12}O_{40}^{3-}$) structure. The magnetic interactions within anions of this series are of interest, since tetranuclear complexes of Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} with the above grouping are hitherto unknown. It may prove possible to prepare mixed-valence and mixed-heteroatom complexes of the types $P_2Co_2^{II}Co_2^{III}W_{18}$ and $P_2Co_2^{II}Ni_2W_{18}$. At this stage the standard error of a determined metal–oxygen bond length is 0·07 Å, but it is already apparent that all bond lengths are similar to those observed in related structures.[5] Average bond lengths (Å) in the Keggin fragments are: 9 W–O (unshared), 1·71; 24 W–O (outer, shared), 1·92; 9 W–O (shared with P), 2·43; 6 W–O (shared with Co), 1·85; 4 P–O, 1·59. The 12 Co–O distances vary from 1·98 to 2·24 Å (average 2·10 Å). The standard deviations of all these averages are entirely consistent with that of an individual determination.

The twelve octahedra adjacent to each PO_4 tetrahedron are linked in the manner of one of the predicted isomers[6] of the Keggin anion, namely that in which one set of three edge-linked octahedra has been rotated by 60°. The rotated set in the present case contains three cobalts. The rotation is needed to make room for the unshared vertices of two CoO_6 groups, which are assumed to be occupied by two water molecules† as is the unshared vertex at Co in the $XCo(H_2O)W_{11}O_{39}^{n-}$ anions (X = Si, P)[2,6] The water in the latter anions is replaceable by, *e.g.*, py or MeCN,[2,6] but the water at Co in the new anions is not replaceable, perhaps because its site is relatively well shielded by oxygen atoms of adjacent WO_6 groups (see Figure). Moreover the close structural relationship between the $XCo^{II}(H_2O)W_{11}O_{39}^{n-}$ and the well-established $XW_{12}O_{40}^{m-}$ anions has no parallel for the new anions, whose 'parent' species $X_2W_{22}O_{70}^{2+}$ (X = P, As) are unknown.

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† *X*-Rays reveal 70, not 68, oxygen atoms in the anion so that two molecules of constitutional water must be present.

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