The Identification and *X*-Ray Structure of the Diphosphatotris(nonatungstophosphato)nonacobaltate(II) Heteropolyanion

Timothy J. R. Weakley

Chemistry Department, Dundee University, Dundee DD1 4HN, U.K.

The $P_5Co_9W_{27}O_{119}H_{17}^{16-}$ anion has $3/m$ symmetry, and contains nine CoO_6 octahedra sharing oxygen atoms with one another and with three α-B PW_9O_{34} moieties and two PO_4 groups.

The title anion is obtained as a by-product (*ca.* 5%) in the preparation of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, of known structure,[1] by the reaction of HPO_4^{2-}, Co^{2+}, and WO_4^{2-} (*ca.* 1:2:9) in hot aqueous solution near pH 7. The addition of KCl precipitates a mixture of salts, from which the salt of $P_5Co_9W_{27}O_{119}H_{17}^{16-}$ is extracted with warm water (40 °C). Other salts (Rb, Cs, guanidinium), which cannot be completely freed from cationic Co, are obtained by metathesis. The least unsatisfactory for crystallographic purposes is the Rb salt (deep rose-pink capped hexagonal prisms), which diffracts sharply although with a very marked decline in scattering intensity with increasing θ to give a data set just large enough for the determination of the main features of the structure of the anion.†

The anion has crystallographic symmetry $3/m$–C_{3h} (Figure 1). The nine CoO_6 octahedra at the core are linked by edge-sharing in three sets of three, with corner-sharing between the sets. Each set shares six oxygen atoms with a $PW_9O_{34}^{9-}$ moiety (α-B isomer[2]) and also shares an oxygen atom with each of two additional PO_4 tetrahedra which lie on the triad axis above and below the equatorial plane. The anion can alternatively be described as consisting of three $PCo_3W_9O_{40}$ units with the α-Keggin[3] (α-$PW_{12}O_{40}^{3-}$) structure, in which the Co atoms occupy adjacent edge-sharing octahedra; these units share oxygens so that the terminal O atom on Co(2) is coincident with the Co(1)–O–Co(1′) bridging atom in the next unit, while other Co–O–Co oxygens on the periphery are shared with the axial phosphorus atoms. With the assignment of the terminal oxygen on Co(1) as H_2O, and the terminal oxygens on the axial P atoms and also the oxygens shared between $PCo_3W_9O_{40}$ groups as OH, the anion has the composition $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$.‡ The bond lengths are in the ranges: W–O(terminal), 1.59—1.83, av. 1.71; W–O(W), 1.79—2.03, av. 1.95; W–O(W.P), 2.35—2.62, av. 2.45; W–O(Co), 1.68—1.74, av. 1.71; Co–O, 1.97—2.18, av. 2.10; P–O, 1.51—1.61, av. 1.56 Å, with standard deviations of 0.05—0.10 Å. The average values are similar to those found[1] for $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, although in the latter the set of three edge-sharing CoO_6 octahedra capping each PW_9O_{34}

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† *Crystal data:* $Rb_{15.6}Co_{0.2}[P_5Co_9W_{27}O_{119}H_{17}].30H_2O$, $M = 9457$, hexagonal, space-group $P6_3/m$, $a = 20.243(8)$, $c = 20.343(6)$ Å, $U = 7219.3$ Å^3, $Z = 2$, $D_c = 4.35$ g cm^{-3}; Mo-K_α radiation (λ = 0.71069 Å), μ = 282 cm^{-1}. Enraf-Nonius CAD-4 diffractometer; cell dimensions from 25 reflections, $12 \leqslant \theta \leqslant 13°$; ω–2θ scan, $1 \leqslant \theta \leqslant 18°$; merging R 0.079 for 1732 unique data, 1058 data with $|F| > 3\sigma(F)$ used in refinement; W, Co, P from E-map (SHELX-76[8]), O, Rb from difference syntheses; final R 0.093, $R_w = [\Sigma\omega(\Delta F)^2/\Sigma\omega F_0^2]^{\frac{1}{2}} = 0.106$ (unit weights, W anisotropic, 166 parameters); the final difference synthesis indicated many disordered lattice water molecules with partial site occupancy but no anomalies within the anion itself. The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

‡ A satisfactory elemental analysis was obtained.

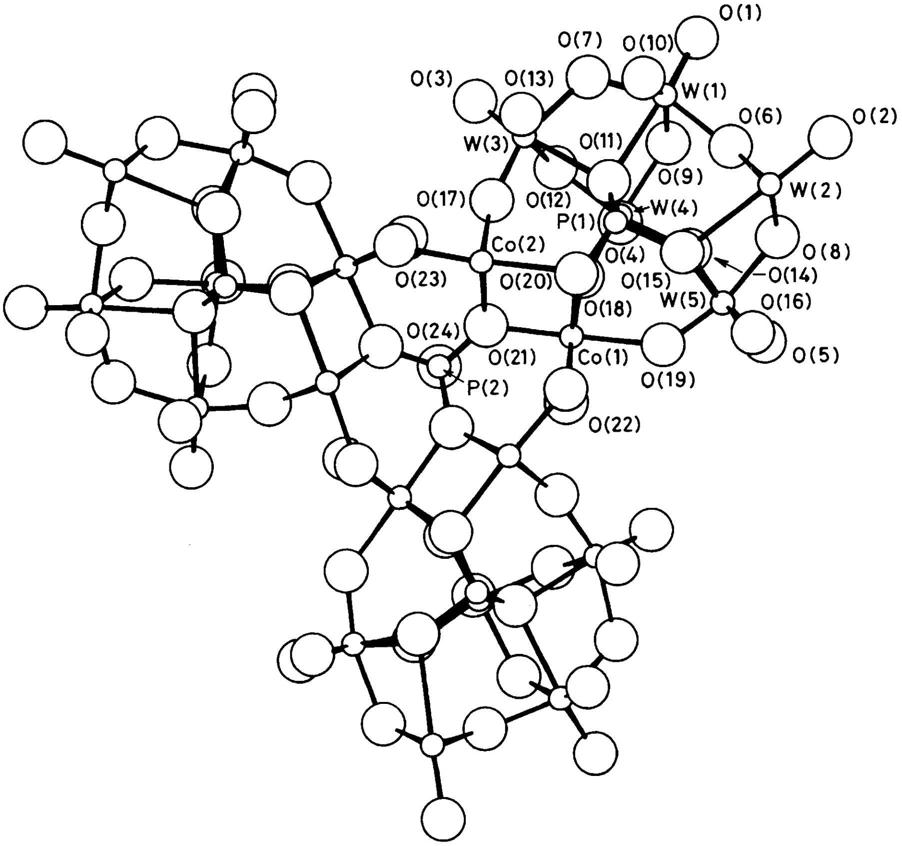

Figure 1. Half the $P_5Co_9W_{27}O_{119}H_{17}^{16-}$ anion, viewed along the three-fold axis from the equatorial mirror-plane. Atoms W(2), P(1), Co(2), O(2,10,13,15,16,20,23) lie in the mirror-plane.

moiety has been rotated 60° to complete a β-Keggin rather than an α-Keggin cluster.

We are still seeking an improved preparation of the new anion which might be extended to analogues containing Zn, *etc.*, in place of Co. If the above reaction mixture is richer in Co^{2+} and HPO_4^{2-} much hydrous Co^{II} phosphate is formed and the yield of the desired anion is not improved. The reaction of pre-formed $PW_9O_{34}^{9-}$ and Co^{2+}(aq.) in 2 : 1 mol ratio is reported[4] to give $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ in good yield. We observe that in the presence of free HPO_4^{2-} and excess of Co^{2+} the new complex is also formed in low yield but, again, the accompanying amorphous material is difficult to remove by filtration. Meanwhile, we believe that other, related types of heterpolyanion should also prove to be preparable.

(i) An alkyl or aryl group should be able to take the place of the terminal oxygen atom of each axial PO_4 group, which is in an open position; the resultant anion would be related to the present one as, *e.g.*, $[(MePO_3)_2Mo_5O_{15}]^{4-}$ is to $[(OPO_3)_2Mo_5O_{15}]^{6-}$.[5]

(ii) An anion $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ has been shown[6] to be an elongated version of $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$. Therefore we predict an anion of abbreviated formula $Co_9P_2(P_2W_{15})_3$, closely related to the present $Co_9P_2(PW_9)_3$ complex.

(iii) The removal of both end-capping sets of linked WO_6 octahedra from α-$P_2W_{18}O_{62}^{6-}$ would afford a $P_2W_{12}O_{50}H_n^{(18-n)-}$ anion, at present unknown (an established P_2W_{12} species is probably[7] derived differently from $P_2W_{18}O_{62}^{6-}$), which would be able to act as a ligand in the manner of $PW_9O_{34}^{9-}$, but at both ends. From this, $[(Co_9P_2)(P_2W_{12})_{3/2}]_n$ polymers in which the Co_9P_2 groups are at the nodes of a three-connected two- or three-dimensional net could be derived {*cf.* the predicted[4] but so far unknown $[Co_4(P_2W_{12})_{2/2}]_n$ relatives of the $Co_4(PW_9)_2$ complex}.

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