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Synthesis and Crystal Structure of Molybdenum-Trisubstituted Tungstophosphate Anion Salt, A-β-$[N(CH_3)_4]_3[PMo_3W_9O_{40}]$

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The molybdenum-trisubstituted tungstophosphate anion, $[PMo_3W_9O_{40}]^{3-}$, was synthesized by a reaction of Na_2MoO_4 and A-$Na_9[PW_9O_{34}]$ in an HCl and 1,4-dioxane mixed solution. X-ray crystal structure analysis of the tetramethylammonium salt of the mixed addenda polyanion revealed the anion geometry as an A-type trisubstituted, β-isomer.

The redox properties of mixed addenda heteropolyanions can be precisely controlled by modifying substituted metal atoms.$^{1)}$ Therefore, the relationships between the structures and the redox properties of such polyanions have attracted much attention in relation to discrete model complexes of mixed metal catalysts.$^{1-4)}$ In the mixed addenda heteropolyanions of the Keggin type, there are numerous possibilities for the positional isomerisms$^{5)}$ as well as the geometrical ones.$^{6)}$ As for the partially substituted heteropolytungstates, their structures in solution, especially the location of the substituted metal atoms, have been confirmed in detail by ^{183}W NMR spectroscopy.$^{7,8)}$ On the other hand, the different addenda atoms in these polyanions are susceptible to disordered arrangements in the solid states$^{9,10)}$ and hence only a few mixed addenda heteropolyanions have been structurally determined by a single crystal X-ray analysis, the sites of the substituted atoms having been disclosed.$^{11-13)}$ In this paper we report the synthesis of the title complex and the substituted sites of Mo atoms in the polyanion structure revealed by X-ray crystallography. This is the first X-ray structural determination for a heteropolyanion containing an A-type trisubstituted, β-isomer of a PW_9 unit.

To an aqueous (35 cm^3) solution of sodium molybdate dihydrate (7.3 g, 30 mmol) was added 50 cm^3 of 12 M HCl (1 M = 1 mol dm^{-3}) and then 50 cm^3 of 1,4-dioxane. To the vigorously stirred solution, freshly prepared A-$Na_9[PW_9O_{34}]\cdot 7H_2O$$^{8)}$ (14 g, 5.5 mmol) was added slowly in small portions (*ca.* 100 mg). After stirring for 1 h at room temperature, solid KCl (3 g) was added to the solution. The resulting yellow precipitates were collected by filtration, washed with a saturated KCl aqueous solution and dried *in vacuo* to afford $K_3[PMo_3W_9O_{40}]$ (12 g, 4.4 mmol). This was dissolved in methanol (300 cm^3) and to the solution was added tetramethylammonium bromide (2.8 g) dissolved in methanol (100 cm^3). The resulting yellow precipitates were collected by filtration, washed with methanol and dried *in vacuo* to afford $[N(CH_3)_4]_3[PMo_3W_9O_{40}]$ (64% yield). It was recrystallized from acetonitrile to give yellow columns. Anal. Found: C, 5.23; H, 1.42; N, 1.40; Mo, 9.6; P, 1.2; W, 56%. Calcd for $C_{12}H_{36}Mo_3N_3O_{40}PW_9$: C, 5.08; H, 1.28; N, 1.48; Mo, 10.15; P, 1.09; W, 58.35%.

The crystal structure of the tetramethylammonium salt was determined by a single crystal X-ray analysis. Crystal data: $C_{12}H_{36}Mo_3N_3O_{40}PW_9$, *F. W.*= 2835.86, orthorhombic, space group $Pmn2_1$, a = 13.844(10), b = 12.871(10), c = 14.687(13) Å, U = 2617(3) Å^3, Z = 2, D_x = 3.598 g cm^{-3}, D_m = 3.60 g cm^{-3}. Intensity data ($2\theta < 50°$) were collected on a Rigaku AFC-5R four-circle diffractometer by the ω-2θ scan technique using graphite-monochromatized Mo-Kα radiation and an absorption correction was applied. The full-matrix least-squares refinements based on 2185 independent reflections with $|F_o| > 3\sigma(F)$ were carried out by assuming anisotropic thermal parameters for W, Mo and P atoms and isotropic ones for O and N atoms and converged to an R factor of 0.094.

Figure 1 shows the polyanion structure of the salt. A crystallographic mirror plane passes through the P, Mo(2), and W(5) atoms. The bond distances are as follows; P-O(internal), 1.50-1.70 Å, M-O(internal), 2.18-2.32 Å, M-O(bridging), 1.42-2.29 Å, M-O(terminal), 1.43-1.90 Å (M = Mo or W). Three Mo atoms belong to three different edge-shared M_3O_{13} groups and are linked to each other through the corner sharing oxygen atom, which is denoted by an A-type positional isomer.$^{7)}$ The possibility of scrambling of Mo and W atoms is excluded by the following findings. A sharp distinction was observed between electron densities on the positions assignable to Mo atoms and those to W atoms. The refinement assuming the atomic scattering factor of tungsten for the Mo positions was not satisfactorily converged with sufficient temperature factors. The edge-shared W_3O_{13} group is rotated by 60° about the threefold axis of the α-isomer, which is denoted by a geometrical β-isomer.$^{6)}$ The present polyanion contains a novel A-β-PW_9 unit,$^{14)}$ which has not been revealed by X-ray crystallography so far, in contrast to an A-α-PW_9 unit observed for some tungstodiphosphates.$^{16-20)}$ The β-isomer of the Keggin anion is generally unstable compared with the corresponding α-one and structural determinations of the β-isomers by a single crystal X-ray analysis have been limited; β_1-$[SiMoW_{11}O_{40}]^{4-}$,$^{9)}$ β-$[SiW_{12}O_{40}]^{4-}$,$^{21,22)}$ and β-$[PMo_{12}O_{40}]^{7-}$.$^{23)}$

To obtain the present A-type trisubstituted, β-isomer of $[PMo_3W_9O_{40}]^{3-}$ anion the addition of 1,4-dioxane to the reaction solution is indispensable, because the isomerization of the mixed addenda polyanion from a β-form to an α-one would be depressed in a mixture of aqueous and organic solutions, as described for the synthesis of β-$[SiW_{12}O_{40}]^{4-}$ anion.[21] Therefore, the A-β-PW_9 configuration of the trivacant precursor, $[PW_9O_{34}]^{9-}$,[24] is retained in the mixed addenda $[PMo_3W_9O_{40}]^{3-}$ anion.

The ^{31}P NMR spectrum[25] of A-β-$[N(CH_3)_4]_3[PMo_3W_9O_{40}]$ in acetonitrile-d_3 showed only a single sharp peak at -7.88 ppm, confirming a single species of the mixed addenda polyanion in solution and occurrence of neither lacunary polyanions nor other isomers. The ^{183}W NMR spectrum[25] in the same solvent showed two sharp peaks at -91.4 and -101.5 ppm with integrated intensities in the ratio 1:2. Both of them were split into narrow doublets by the spin-spin coupling with the ^{31}P nucleus ($^2J_{W-O-P}$ = 1.5 Hz for both the signals). The signal at the higher field can be assigned to the six "belt" W atoms (W(1)-W(3) and W(1')-W(3') in Fig. 1) and the other to the three "cap" W atoms (W(4), W(4'), and W(5)), in comparison with those observed for A-β-$[SiV_3W_9O_{40}]^{4-}$ anion.[7] These spectral patterns are consistent with the molybdenum-trisubstituted tungstophosphate polyanion structure of A-type and β-isomer in solution.

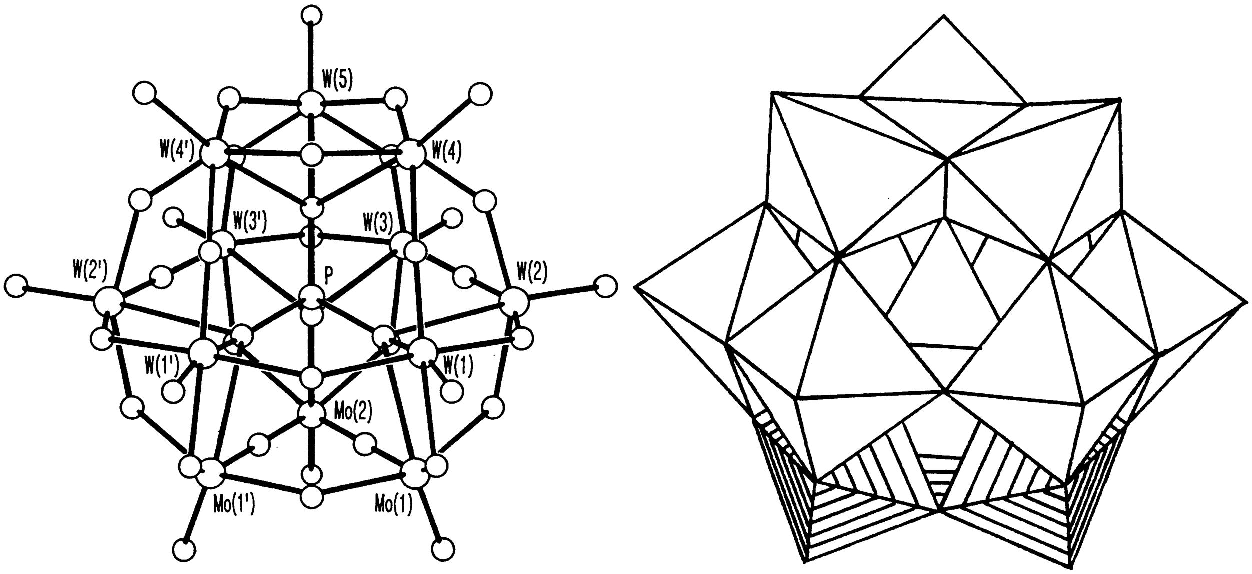

Fig. 1. Molecular geometry of the anion of A-β-$[N(CH_3)_4]_3[PMo_3W_9O_{40}]$; ball and stick (left) and polyhedral (right) representations. Hatched parts indicate MoO_6 octahedra.

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25) Chemical shifts of the ^{31}P and ^{183}W NMR signals were expressed in ppm with negative values upfield from those of external 30% H_3PO_4 and 2 M Na_2WO_4 in D_2O, respectively.

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