

Synthesis, Solution and Solid State Structures, and Aqueous Chemistry of an Unstable Polyperoxo Polyoxometalate: $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$

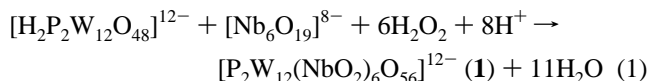
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Received January 31, 1997

The impetus for this work lies both in antiviral chemotherapy and oxidations by the environmentally attractive oxidant H_2O_2 based on early transition metal oxygen anion clusters (polyoxometalates or POMs for short). POMs have significant applications in catalysis (including some processes recently commercialized), medicine, and other areas of current interest.^{1–3} The title POM, $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$ (**1**), was an attractive target for three reasons: First, molecular modeling data indicated it should be a good HIV-1 protease inhibitor, and this has proved to be the case ($IC_{50} = 0.084 \mu M$).⁴ Second, Nb^V -containing POMs are usually more potent antiviral agents and less toxic than their Nb-free analogs.^{5–7} Third, **1** would facilitate evaluation of the structural and chemical features of two or more adjacent (Nb^VO_2) peroxo (henceforth NbO_2) units, a structural element of central significance in synthetic Nb^V chemistry^{8–12} and of potential importance in H_2O_2 activation.¹³ There was concern that **1** could not be prepared as the only clear route to **1** (eq 1), involving a highly labile polytungstophosphate, $H_2[P_2W_{12}O_{48}]^{12-}$,¹⁴ and aqueous H_2O_2 . While H_2O_2 is catalytically activated by some POMs for highly selective oxidation of organic substrates,^{15–18} it rapidly degrades other POMs,

including many polytungstophosphates, to form polyperoxo-metalates, including the catalytically effective and much studied $\{PO_4[WO(O_2)_2]_4\}^{3-}$.^{19–27}



Reaction of $[H_2P_2W_{12}O_{48}]^{12-}$ and $[Nb_6O_{19}]^{8-}$ in aqueous HCl/LiCl forms **1** in 84% yield, indicating that decomposition does not effectively compete with eq 1 under these conditions.²⁸ The initially amorphous **1** contains H_2O_2 and Cl^- which are both removed by size exclusion chromatography of the lithiated complex. Research on **1** is complicated by the fact that it is unstable. While it is much more stable in the presence of H_2O_2 in aqueous solution than in the absence, *it is unstable both in solution and in the solid state*. Recrystallization to obtain both analytically pure bulk material and diffraction quality single crystals of **1** must be conducted in aqueous H_2O_2 .²⁹ The best crystals are formed in the simultaneous presence of Li^+ , K^+ , and Cs^+ .³⁰

The X-ray structure of **1** (Figure 1)³¹ is consistent with the synthesis (eq 1) and the other data discussed below. It derives from the classical Wells–Dawson α - $[P_2W_{18}O_{62}]$ core,³² with a contiguous longitudinal strip of six tungsten terminal oxo groups ($W=O$) (one on each cap position and two on each belt position) replaced by six NbO_2 groups. Each of the six Nb atoms is ligated by four doubly-bridging O atoms, one quadruply-bridging O atom (cap sites) (or triply-bridging O atom on belt sites), and one terminal η^2 -coordinated peroxo unit, while each of the 12 W atoms exhibits the conventional O_6 coordination polyhedra.¹ This η^2 -peroxo-containing distorted pentagonal bipyramidal coordination polyhedron is seen for the metal centers in only one other conventional (highly condensed) polyoxoanion, the β_3 - $[(Co^{II}O_4)W_{11}O_{31}(O_2)_4]^{10-}$ complex of Baker and co-workers.^{33,34} None of the other structurally characterized polyperoxotungstates or polyperoxomolybdates

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(28) Solid α - $K_12H_2[P_2W_{12}O_{48}]$ (12.15 g, 3.5 mmol) was added to 450 mL of an aqueous solution 6.7 mM in $K_2H[Nb_6O_{19}]$, 0.5 M in H_2O_2 , 1 M in LiCl, and 4 M in HCl. After of the solid dissolved, 15 mL of 4 M HCl was added (final pH = 0.85). Next, KCl (15 g, 0.201 mol) was added, the mixture was stirred for 5 min and then H_2O_2 (5 mL of 11.6 M) was added. The solution was filtered, and then CsCl (3 g, 0.0178 mol) was added resulting in 3.89 g of an amorphous yellow precipitate. Additional product was obtained by subsequent concentration and refrigeration (total yield 11.08 g, 84% based on $[Nb_6O_{19}]^{8-}$).

(29) Anal. Found (calcd) for $Li_{1.5}K_{3.5}[P_2W_{12}(NbO_2)_6O_{56}] \cdot H_2O$: H, 0.60 (0.65); Li, 0.84 (0.89); O (by difference), 30.70 (29.84); Cl, 0 (0); K 2.73 (2.73); Nb, 12.23 (13.00); W, 52.01 (51.44). The analyses for P on several samples varied from 0.88 to 1.10 (theoretical is 1.28).

(30) X-ray quality crystals of **1** were grown by dissolving 1.00 g (0.228 mmol) of **1** in 5 mL of 0.05 M H_2O_2 containing 0.290 g (7.27 mmol) of $LiClO_4$. After the precipitate was filtered, the supernatant was put into a small vial, and solid CsCl (0.090 g, 0.53 mmol) was added. After more yellow precipitate was filtered, the supernatant was concentrated over 1 week at 25 °C to form crystals.

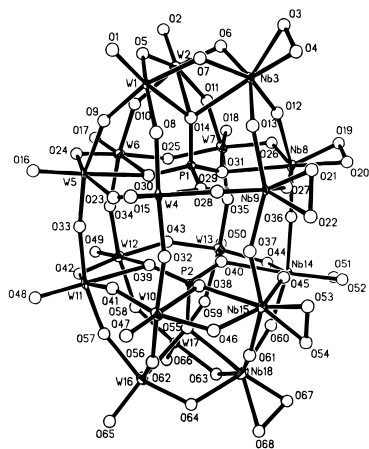


Figure 1. The structure of $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$, **1**. W1, W4, W5, W10, W11, and W16 have ca. $5/6$ W + ca. $1/6$ Nb character; Nb3, Nb8, Nb9, Nb14, Nb15, and Nb18 have ca. $5/6$ Nb + ca. $1/6$ W character. Selected average bond lengths (Å) and bond angles (deg): W–O_t, 1.73 (3); W–O_b, 1.92 (2); W–O_{b'}, 1.87 (2); W–O_c, 2.41 (2); W–O_d, 2.39 (2); Nb–O_b, 1.95 (2); Nb–O_{b'}, 2.04 (2); Nb–O_p, 1.93 (3); Nb–O_c, 2.35 (2); O_p–O_p, 1.43 (4); P–O_c, 1.53(2); P–O_d, 1.59 (2); O_p–Nb–O_p, 43.7(12), where O_t = terminal oxo, O_b = doubly-bridging oxo, O_{b'} = doubly-bridging oxo between W and Nb, O_c = triply-bridging oxo, O_d = quadruply-bridging oxo, and O_p = peroxo oxygen.

have a conventional polyoxometalate structure.^{26,33} The average O_p–O_p distance in **1** (1.43 Å) is slightly shorter than that for noncoordinated O₂²⁻ (1.49 Å)³⁵ and is mainly attributed to the decrease in repulsion between the lone electron pairs on each oxygen in O₂²⁻. The average Nb–O_p distance of 1.93 Å is 0.1 Å shorter than that in the monomeric tetraperoxo niobium complex, $[Nb(O_2)_4]^{3-}$,^{36,37} while the average O_p–Nb–O_p angle of 43.7° is close to that in $[Nb(O_2)_4]^{3-}$ (43.3°). The relative orientations of the NbO₂ units at the belt positions is noteworthy; two of them (Nb8,O19,O20 and Nb14,O51,O52) lie in the plane defined by the W₄Nb₂ belts, while the other two (Nb9,O21,O22 and Nb15,O53,O54) lie perpendicular. The arrangement of peroxo groups most likely derives from cation–anion interactions in the crystal lattice (e.g., Cs7, O22, and O53 are within van der Waals radii of each other) and the coordination geometrical requirements around the metals (see Supporting Information). The orientation of the NbO₂ units lowers the polyanion symmetry to C₁.

(31) Crystal data for (H₃C₈S₅K₃Li_{0.3})[P₂W₁₂(NbO₂)₆O₅₆]·11H₂O: orange-yellow crystal, dimensions 0.02 × 0.02 × 0.05 mm, monoclinic space group P2₁/c, with *a* = 13.5718(2) Å, *b* = 22.0858(1) Å, *c* = 24.0698(3) Å, β = 96.675(1)°, *V* = 7165.87(14) Å³, *D_c* = 4.617 g cm⁻³, *Z* = 4. The data were collected on a Siemens SMART system using Mo Kα radiation (λ = 0.71073 Å) and corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-square on F² techniques using SHELXTL V5.03 with anisotropic temperature factors for all W, Nb, Cs, K, and Li atoms and isotropic temperature factors for the remaining atoms. As some of the metal sites within the polyanion and cation positions were severely disordered, a common situation for crystal structures of such complexes (cf. Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1235–1241, footnote 13), mixed form scattering factors, and unit occupancies with common coordinates and anisotropic parameters were employed for those atoms during refinement. As a result of orientational disorder at ca. 15% of the sites in the polyanion **1**, the Nb atoms are at heavy-atom positions 1, 4, 5, 10, 11, and 16, and at ca. 85%, they are at positions 3, 8, 9, 14, 15, and 18. At final convergence, *R*₁ = 9.65% and GOF = 1.166 based on 9092 reflections with *F*_o > 4σ(*F*_o).

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The ³¹P (1 peak; δ rel to 85% H₃PO₄/D₂O = –7.99 ppm) and ¹⁸³W (3 peaks of equal area; δ rel to 2 M Na₂WO₄ in D₂O = –122.4, –158.1, and –203.5 ppm) NMR spectra indicate that **1** has effective C_{2v} symmetry in solution (see Supporting Information). Fast rotation on the NMR time scale of each peroxo unit about the axis through each Nb and the center of the O–O bond would explain the apparent increase in symmetry from C₁ to C_{2v}, but this is quite unlikely given both the small thermal ellipsoids of the peroxo oxygens (Figure 1; see Supporting Information) and the NMR line widths (see Supporting Information). Fast exchange between peroxide bound to Nb and in solution could also explain the spectra but this can be ruled out from the half-life of **1** in H₂O₂-free H₂O (ca. 12 h). The likely explanation for the NMR spectra is that a number of orientational isomers with respect to the NbO₂ units is present but that peroxo orientation has a minimal impact on the NMR spectra. The ν O–O, ν_{sym} NbO₂, and ν_{asym} NbO₂ are resolved stretches at 872, 666, and 596 cm⁻¹, respectively, in the infrared, consistent with η²-peroxo groups.³⁷

The NbO₂ groups in **1** can be reduced by several reagents in H₂O to the corresponding terminal Nb^{VO} groups which can undergo dimerization via Nb–O–Nb linkages (both processes are already documented for NbO₂ or NbO groups in polyanions).^{8,9} Iodometric titration of **1** yields 6.2 ± 0.4 NbO₂ groups. Reduction of **1** by NaHSO₃ is nonselective resulting in many species including dimeric polyanions indicated both by negative ion FAB-MS³⁸ and IR (the 682 cm⁻¹ stretch characteristic of linear Nb–O–Nb is formed).⁸ While the FAB-MS technique itself can lead to dimerization of monomeric Nb–polyoxometalates,³⁹ the results with **1** are unequivocal: **1**, either in H₂O₂-free solution or in the solid state, decomposes to the corresponding P₂W₁₂(NbO)_{*x*}(NbO₂)_{6–*x*}, *x* = 1–6, species that dimerize.⁴⁰ In contrast, **1**, in 0.5 M aqueous H₂O₂, is relatively stable up to pH 10.7. Furthermore, the FAB-MS of such samples exhibit no peaks indicative of dimers; only those of monomeric **1** are present. Reduction of **1** by hydroquinone or DMSO is selective. Initially a new species with only one ³¹P NMR peak (0.2 ppm downfield from **1**) and four NbO₂ groups from iodometric titration is produced. After several days, both reductants produce many species with a net of <1 NbO₂ per equivalent of initial **1** remaining. The data are consistent with rapid selective reduction of the cap NbO₂ groups followed by slow reduction of the belt NbO₂ groups and implicate that the cap (α₂) position of the classical Wells–Dawson polyanion is less sterically encumbered than the belt (α₁) position.⁴¹ In summary, both FAB-MS and IR data show that **1** does not form dimers above pH 8 or in the presence of H₂O₂.

Acknowledgment. We thank NIH (R01 AI32903), NSF (CHE-9412465), and MBI/ONR (N00014-95-1-116) for support and Helga Cohen of the U. of So. Carolina NMR Center for ¹⁸³W NMR spectra. We acknowledge the use of Shared Instrumentation provided by NIH and NSF and thank Fred Strobel for the FAB-MS.

Supporting Information Available: Complete listing of structure determination summary, atomic coordinates and isotropic displacement coefficients, bond lengths and angles, and anisotropic displacement parameters and figure showing NMR spectra of **1** (12 pages). See any current masthead page for ordering and Internet access instructions.

JA970329T

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(40) Species with *m/z* = 7820–7908 repeatedly form. Note, the molecular weight of the monomeric (NbO)₆ polyanion, [P₂W₁₂Nb₆O₆₈]¹²⁻, is 3914.2 and that of the dimeric anion, [(P₂W₁₂Nb₆O₆₆)₂O]²³⁻, is 7780.4 (assuming one NbO₂ group from each anion is reduced to a NbO group and the two molecules dimerize through this group). All attempts to isolate the (NbO)₆ analog of **1** have been precluded by formation of dimers.

(41) A confirming experiment involves the recently prepared and fully characterized monoperoxo complexes α₁- and α₂-K₇[P₂W₁₇(NbO₂)O₆₁]; the peroxo function of the α₂ isomer reduces significantly faster than that of the α₁ isomer (see ref 4).