specific cyclization (KOH, then HCl in methanol) of **16b** and **17b** and subsequent acetonization afforded **18b** and **19b**,[20] respectively in 90–95% yield.[21] Stereochemical assignments could be made at this stage through a combination of high-field ^{1}H NMR experiments (NOE difference and *J* value measurements). The results of these analyses and the crystallographic data are included in the Supplementary Material.

Further studies directed toward the synthesis of polyether ionophores are currently under way.

Acknowledgment. This investigation was supported by the NIH (GM-30738), NSF (Presidential Young Investigator Award), and Pfizer Incorporated, to whom we are grateful. Fellowship support (for T.S.) was contributed by the Berlex Laboratories in the form of a Berlex Predoctoral Fellowship. We thank Dr. Simon K. Kearsley for the use of the UPLOT structure plotting package.

Supplementary Material Available: A description of the methods employed to determine stereochemistry including ^{1}H NMR, ^{13}C NMR, IR, and MS data and experimental procedures (11 pages). Ordering information is given on any current masthead page.

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(20) Similar results were obtained in the cyclization and acetonization of **16a** and **17a** to provide **18a** and **19a**, respectively (β-methyl (of dioxane) = H).

(21) (a) Schultz, W. J.; Etter, M. C.; Pocius, A. V.; Smith, S. *J. Am. Chem. Soc.* **1980**, *102*, 7981. (b) Simmons, H. E.; Maggio, J. E. *Tetrahedron Lett.* **1981**, *22*, 287. (c) Paquette, L. A.; Vazeux, M. *Tetrahedron Lett.* **1981**, *22*, 291. (d) Dolle, R. E.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1985**, *107*, 1691. (e) Hoye, T. R.; Suhadolnik, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5312.

Synthesis and Structural Characterization of the First Phosphorus-Centered Baker–Figgis γ-Dodecametalate: γ-$\mathrm{Cs_5[PV_2W_{10}O_{40}]\cdot \mathit{x}H_2O}$

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Phosphotungstates form a large class of heteropolyanions,[1] yet, surprisingly, only the α-form (Keggin structure) of dodecahedral $\mathrm{PX_yW_{12-y}O_{40}}^{n-}$ species has been reported. In contrast, both the α- and β-Baker–Figgis isomers[2] of the corresponding silicates and germanates are known.[3] Recent work by us and others[4] has demonstrated the utility of lacunary (defect) polyoxoanions as precursors for the synthesis of specifically substituted larger polyanions; the fragments serve as ligands for other heteroatoms.

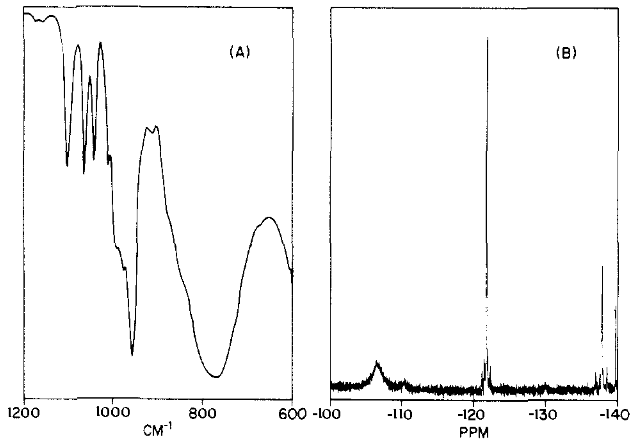

Figure 1. (A) IR spectrum (mineral oil mull) of γ-$\mathrm{Cs_5[PV_2W_{10}O_{40}]\cdot 6H_2O}$. (B) ^{183}W NMR spectrum of 200 mg of $\mathrm{NaVO_3}$, pH 2, 5 g of γ-$\mathrm{Li_5[PV_2W_{10}O_{40}]}$ in 13 mL of $\mathrm{D_2O}$, 5 °C, in a 20-mm vertical probe, 80000 shots, total time 64 h, resolution enhanced to reveal $^2J_{\mathrm{WOW}}$ satellites. The low-intensity resonance at −139.7 ppm is an unidentified pernicious impurity (ca. 2%, $\mathrm{W_{10}}$).

Here we report the first Baker–Figgis γ-isomer[5] of a dodecahedral phosphotungstate species derived from the lacunary precursor[6] $\mathrm{Cs_7[PW_{10}O_{36}]}$ and characterization by ^{183}W, ^{51}V, and ^{31}P NMR, IR spectroscopy, and X-ray crystallography.

Slow addition of up to 0.5 equiv of solid $\mathrm{Cs_7[PW_{10}O_{36}]\cdot \mathit{x}H_2O}$ to a preformed solution of $\mathrm{VO_2}^+$ at pH 0.8 yields an instantaneous precipitate[7] of γ-$\mathrm{Cs_5[PV_2W_{10}O_{40}]\cdot \mathit{y}H_2O}$. Monitoring of the reaction by ^{51}V NMR shows a regular decrease in the intensity of the $\mathrm{VO_2}^+$ resonance (−543.9 ppm) and the appearance of a weak resonance of essentially constant intensity (−570.3 ppm) due to the sparingly soluble product. Isolated solid shows a single ^{51}V NMR line[8a] (−547.1 ppm, $\Delta\nu_{1/2}$ = 112 Hz, pH 2.5, 30 °C) which is gradually replaced[8b] ($t_{1/2}$ ca. 7 h) by a pair of equal-intensity lines due[8c] to a β-$\mathrm{PV_2W_{10}O_{40}}^{5-}$ species. In spite of the limited stability of the pure γ-compound, the material is substantially stabilized in the presence of an excess of $\mathrm{VO_2}^+$. Suitable X-ray quality crystals were grown[9] from a 50 mol %, pH 2 solution of $\mathrm{VO_2}^+/\gamma$-$\mathrm{Cs_5[PV_2W_{10}O_{40}]}$ chilled to 0 °C. Microanalytical data were obtained on these crystals.

The IR spectrum (Figure 1A) is similar to that of other α-$\mathrm{PV_2W_{10}O_{40}}^{5-}$ compounds,[4a,b] and the precursor $\mathrm{PW_{10}O_{36}}^{7-}$. A notable difference is the decrease in frequency of the ca. 900-cm^{-1}

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(1) See: Pope, M. T. "Heteropoly and Isopolymetalates", Springer-Verlag: New York, 1983, pp 65–72.

(2) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794–3797.

(3) See, for example: (a) Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999–1002. (b) Hervé, G.; Tézé, A. *Inorg. Chem.* **1977**, *16*, 2115–2117. (c) Robert, F.; Tézé, A.; Hervé, G.; Jeannin, Y. *Acta Crystallogr., Sect. B* **1980**, *B36*, 11–15. (d) γ-$\mathrm{XV_2W_{10}O_{40}}^{6-}$ (X = Si, Ge), which are analogous to the phosphorus species reported here, are mentioned in a meeting abstract but without details of synthesis or structure verification. Tézé, A.; Canny, J.; Leyrie, M.; Hervé, G. "Abstracts, Polyoxometallate Workshop"; St. Lambert-des-Bois, France, July, 1983.

(4) (a) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677–7687. (b) Domaille, P. J.; Watunya, G. *Inorg. Chem.*, submitted for publication. (c) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1984**, *4*, 62–68. (d) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286–4292. (e) Mossoba, M. M.; O'Connor, C. J.; Pope, M. T.; Sinn, E.; Hervé, G.; Tézé, A. *J. Am. Chem. Soc.* **1980**, *102*, 6864–6866. (f) Ortega, F.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 3292–3297. (g) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274–7277. (h) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006–1008. (i) Finke, R. G.; Droege, M. W.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587–1589. (j) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.*, in press.

(5) The γ-isomer reported here is not to be confused with the notation in a recent crystal structure: (a) Fuchs, J.; Thiele, A.; Palm, R. *Angew Chem., Int. Ed. Engl.* **1982**, *23*, 789–790. (b) A more recent interpretation of the X-ray data refutes the existence of the reported octahedral symmetry species: Evans, H. T.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501–504. Our structure is a true Baker–Figgis γ-isomer based upon simultaneous 60° rotations of two adjacent $\mathrm{M_3O_{13}}$ units of the tetrahedral Keggin structure.[3d]

(6) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 1865–1867.

(7) $\mathrm{NaVO_3}$, 1 g (8.2 mmol), was dissolved in 40 mL of hot water. Upon cooling, 3 M HCl was added dropwise to reduce the pH to 0.8. Small (10 mg) portions of $\mathrm{Cs_7[PW_{10}O_{36}]}$ were added with vigorous stirring until a total of 12.5 g (3.6 mmol) had accumulated. After stirring for 30 min the solution was filtered to give 10.9 g of yellow powder (ca. 90%).

(8) (a) The position of the ^{51}V NMR resonance of the γ-isomer is pH-dependent. (b) Because of the stabilization by $\mathrm{VO_2}^+$, rate parameters are dependent upon compound purity. The 7-h half-life was observed in unbuffered solution at pH 2.5. (c) The characterization of β-$\mathrm{PV_2W_{10}O_{40}}^{5-}$ will be detailed in a forthcoming publication. Strong initial evidence is provided by the ^{51}V NMR spectrum. Two distinct lines (−544.4 and −555.2 ppm, pH 3.5, 30 °C) with non-Lorentzian line shapes are observed, indicating the presence of scalar coupling with $^2J_{\mathrm{VOV}} \sim 20$ Hz. Confirmation is obtained by 2D ^{51}V COSY NMR.[4a]

(9) $\mathrm{NaVO_3}$, 100 mg, was dissolved in 100 mL of water and adjusted to pH 2 with 3 M HCl. γ-$\mathrm{Cs_5[PV_2W_{10}O_{40}]\cdot \mathit{x}H_2O}$, 5 g, was added and the mixture stirred for 30 min. Filtration through analytical filter aid produces a clear yellow solution which is chilled at 0 °C for 12 h to produce pale yellow crystals suitable for X-ray analysis. Prolonged chilling produces a total of 2.4 g of product which analyses for $\mathrm{Cs_5[PV_2W_{10}O_{40}]\cdot 6H_2O}$. Calculated (Found): Cs, 19.6 (19.0); P, 0.92 (0.72); V, 3.01 (3.27); W, 54.3 (54.1); O, 21.8 (22.8); H, 0.36 (0.44); $\mathrm{H_2O}$, 3.2 (3.2). Water content in the X-ray crystals will differ because of different drying procedures.

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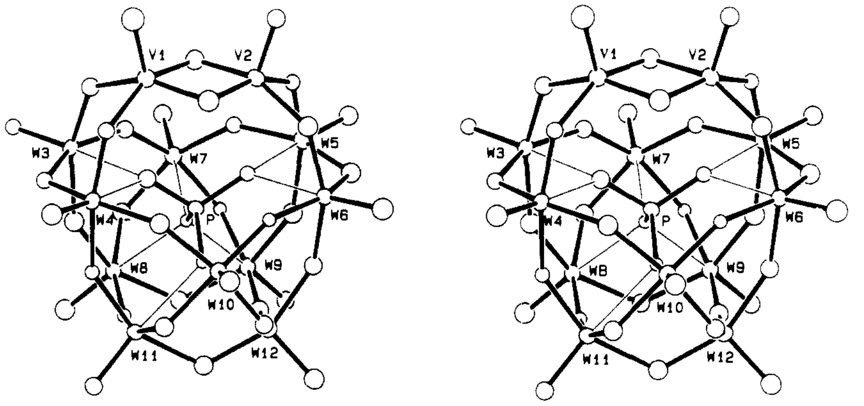

Figure 2. Stereodrawing of the $[PV_2W_{10}O_{40}]^{5-}$ anion. The long W-O(phosphate) bonds have been drawn as lines; the even longer V-O(phosphate) bonds are not shown. Although the differences are not significant on the basis of their esd's, the P-O bond lengths appear to be sensitive to the number of metal atoms to which the oxygen atoms are bound: 1.54 (2) and 1.56 (2) Å for the two oxygens that are bonded to three tungsten atoms vs. 1.52 (2) and 1.52 (2) Å for the two that interact with only two tungsten atoms. The V=O bond lengths are 1.61 (2) and 1.63 (2) Å for V(1) and V(2), respectively; the V—O—V bonds vary from 1.79 (2) to 1.87 (2) Å.

band, generally ascribed to M-O-M corner vibrations, to overlap with the 800-cm^{-1} M-O-M edge vibration.[10]

The ^{31}P NMR spectrum of γ-$PV_2W_{10}O_{40}{}^{5-}$ shows a single line at −14.56 ppm while the precursor $PW_{10}O_{36}{}^{7-}$ has a single (solid state) resonance at −12.5 ppm. The ^{183}W NMR spectrum (Figure 1B) shows a three-line 4:4:2 pattern with the high-frequency line (−106.2 ppm) substantially broadened[4a] by scalar coupling to the quadrupolar relaxed ^{51}V. Decoupling of ^{51}V sharpens this line, and $^2J_{WOW}$ values establish the expected connectivity and assignment.[11] Nevertheless, the high symmetry of the anion, and resultant paucity of ^{183}W features, left some doubt in the formulation so an X-ray crystal structure determination was made.

The structure is shown in the stereoperspective of Figure 2[12] and unequivocally establishes the γ-nature of the compound.

The tungsten atoms exhibit typical distorted octahedral coordinations with short W=O (terminal) bonds, 1.69–1.74 Å, long W—O (phosphate) bonds, 2.34–2.43 Å, and intermediate W—O—M bonds, 1.85–2.00 Å for M = W and 1.82–1.86 Å for M = V. The exceptionally long V—O (phosphate) bonds, 2.70 (2) and 2.64 (2) Å for V(1) and V(2), respectively, place the coordinations of the vanadium atoms in between the 6-fold distorted octahedron expected for the γ-isomer and that of a truly isolated 5-fold square prism. The vanadium atoms are also unique in the sense that their VO_n polyhedra are joined together by a single shared edge, which is the only shared edge joining adjacent M_3O_{13} units in the complex.

Isolation and identification of this thermodynamically unfavored isomer from a well-defined precursor defect anion again demonstrate the utility of these species in the synthesis of novel heteropolyanion systems. Furthermore, a synthetic scheme that produces a less favored isomer allows entry into other species which are thermodynamically downhill. The facile reaction with $VO_2{}^+$ (coupled with the monitoring of reactions by ^{51}V NMR) suggests that poorly defined precursor anions may be identifiable from final products.

Acknowledgment. Fine technical assistance was provided by G. Watunya and L. Lardear.

Registry No. $Cs_5[PV_2W_{10}O_{40}]\cdot 8H_2O$, 100513-51-7; $Cs_7[PW_{10}O_{36}]$, 100513-52-8; $VO_2{}^+$, 18252-79-4.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and selected bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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(10) Better resolved IR spectra are obtained from the tetra-*n*-butylammonium salt where the M-O-M corner vibration is evident at 874 cm^{-1}. Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207–216.

(11) ^{183}W NMR data (5 °C) −137.1 (2 W, $^2J_{WOW} = 23.7 \pm 0.2, 6.4 \pm 0.2$ Hz), −121.1 (4 W, $^2J_{WOW} = 17.0 \pm 0.2, 6.6 \pm 0.2$, $^2J_{POW} = 1.28$ Hz), −106.2 ppm (4 W, $^2J_{WOW} = 22.7 \pm 2, 17.2 \pm 2$ Hz).

(12) Crystal structure information: $Cs_5[PV_2W_{10}O_{40}]\cdot 8H_2O$, FW = 3419.98. Monoclinic, space group $C2/c$. At −100 °C, $a = 32.151$ (8) Å, $b = 18.343$ (4) Å, $c = 17.637$ (4) Å, $\beta = 120.78$ (1)°, $V = 8936.2$ Å^3; $D_X = 5.084$ g cm^{-3}; $\mu = 307.2$ cm^{-1}. Data were collected on a Syntex P3 diffractometer with the crystal cooled to −100 °C (graphite monochromator, MoKα radiation, $\lambda = 0.71069$ Å). Intensity data for 7855 reflections were collected by using the ω-scan technique (4° < 2θ < 50°; scan width of 1.0°; variable scan rate of 5.0–15.0° min^{-1}). On the basis of ψ-scan data, empirical absorption corrections ranging from 0.56 to 1.00 were applied. Following solution (heavy-atom technique) and isotropic refinement, DIFABS (Wacker, N.; Stuart, P. *Acta Crystallogr., Sect. A* **1983**, *A39*, 159) indicated that further absorption corrections were necessary and these were applied: 0.80–1.15. Full-matrix, least-squares refinement of 372 variables (W, Cs, V, and P with anisotropic thermal parameters; O with isotropic) using 5193 reflections for which $I > 3.0\sigma(I)$ converged at $R = 0.047$. Three of the Cs^+ ions are in partially occupied sites with water molecules occupying these sites when Cs^+ does not; the occupancies were included in the refinement. The final difference map had a number of peaks in the range 1.0–1.2 e Å^{-3} which were located near heavy atoms. All computer programs used are local modifications of the programs supplied by the Enraf-Nonius Corp. (Frenz, B. A. "Computing in Crystallography"; Schenk, H.; Olthof-Hazehamp, R., van Koningsweld, H., Bassi, G. C. Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71).

Deuterium Isotope and Anomeric Effects in the Conformational Equilibria of Molecules Containing CHD-O Groups

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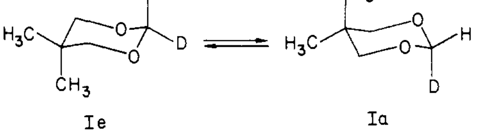
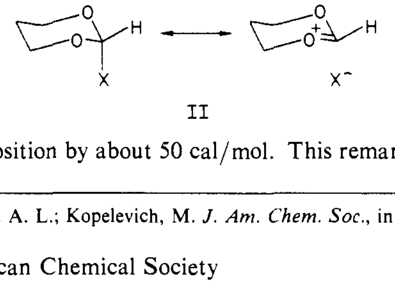
We have recently shown that the deuterium in a CHD group in cyclohexane-d_1 or cyclohexane-d_{11} prefers the equatorial over the axial position by 6.3 ± 1.5 cal/mol.[1] We now report that the deuterium in 5,5-dimethyl-1,3-dioxane-2-d_1 (I) prefers the



Ie Ia



II

equatorial position by about 50 cal/mol. This remarkably large

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[1] Anet, F. A. L.; Kopelevich, M. *J. Am. Chem. Soc.*, in press.