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Confirmation of the Semivacant Wells–Dawson Polyoxotungstate Skeleton. The Structures of $[Ce\{X(H_4)W_{17}O_{61}\}_2]^{19-}$ (X = P, As) Indicate the Probable Location of Internal Protons

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Reaction of Ce(III) with lacunary versions of $[H_4XW_{18}O_{62}]^{7-}$ (X = P, As) yields the 1:2 complexes $[Ce(H_4XW_{17}O_{61})]^{19-}$ (X = As, **1**; P, **2**) in good yield, characterized in solution and the solid state by NMR spectroscopy and X-ray crystallographic analysis, respectively. The structures confirm a syn C_2 conformation that is analogous to that observed for $[Ln(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$ but with “empty” O_4 tetrahedra that are in positions remote from the cerium atom. Bond valence sum calculations for these structures show that the four protons that are required for charge balance in all salts of the XW_{18} anions and their lacunary derivatives are almost certainly bound to the oxygen atoms of the empty tetrahedra.

In addition to the variety of structures and unusual combinations of properties that lead to applications in many fields, polyoxometalates[3] can illustrate unique protonation chemistry. This is best exemplified by the metadodecatungstate anion α-$[(H_2)W_{12}O_{40}]^{6-}$, which has long been known[4] to be isostructural with other Keggin-structure heteropolyanions such as $[PW_{12}O_{40}]^{3-}$. The metatungstate protons are quantifiable by ^{1}H NMR spectroscopy in aqueous solution,[5,6] an observation that is consistent with their location *within* the central O_4 tetrahedron of the Keggin structure. Metastable $[(H)W_{12}O_{40}]^{7-}$ (and various fluoro-metatungstates incorporating a single central proton) have also been characterized by ^{1}H NMR spectroscopy in aqueous solution.[7] More recently, Himeno et al.[8] isolated from aqueous acetonitrile solution the tetra-*n*-propylammonium salt of an anion formulated as $[H_4W_{12}O_{40}]^{4-}$ that, according to ^{1}H NMR spectroscopy contains (in CD_3CN) four nonexchangeable and, it was concluded, *central* protons.

Potassium salts of the new tungstophosphate anions $[H_4PW_{18}O_{62}]^{7-}$, $[H_4PW_{17}O_{61}]^{11-}$, and $[Zn(H_2O)H_4PW_{17}O_{61}]^{9-}$ were first synthesized and characterized by P and W NMR spectroscopy by Contant et al. in 2000.[9] It was proposed that the anions, *all of which required four protons for charge balance*, had the same oxometalate skeleton as the well-known Wells−Dawson anions (e.g., α-$[P_2W_{18}O_{62}]^{6-}$) and their lacunary derivatives, although it proved impossible at that time to confirm this by X-ray crystallography. Subsequent synthetic and electrochemical investigations of these and related 17- and 18-tungstoarsenate derivatives[9−11] were all interpreted assuming a Wells−Dawson structure in which one P or As atom is missing. It could be speculated that some or all of the four protons required for charge balance were contained within the vacant tetrahedral O_4 cluster in much the same way as the central two protons in the metatungstate anion. No ^{1}H signals were observed for the H_4XW_{18} anions in aqueous solution,[9] which implies fast exchange with solvent protons.[12] However, when $[H_4AsW_{18}O_{62}]^{7-}$ was transferred into benzene-d_6 following the method of Katsoulis and Pope,[13] the solution yielded a 300-MHz ^{1}H NMR spectrum with a signal at 5.31 ppm [in addition to the spectrum resulting from the cation (∼1.1−3.3 ppm)]. The

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(3) For recent reviews, see: *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Pergamon Press: Oxford, U.K., 2004; Vol. 4, pp 635−678 (Pope, M. T. Polyoxoanions: Synthesis and Structure) and 679−759 (Hill, C. L. Polyoxometalates: Reactivity).

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integrated intensity of the 5.31-ppm resonance was compared with that of a known quantity of 1,2-dichloroethane (3.37 ppm) in the same solution and corresponded to the expected four protons per AsW_{18}.[14]

Attempts to solve the structures of various XW_{18} salts by X-ray crystallography have hitherto been unsuccessful, and in any case, if the Wells−Dawson framework were to be adopted by these anions, it is likely to be crystallographically disordered with half-occupancy of X at both tetrahedral sites. We have therefore synthesized and characterized salts of $[Ce^{III}(XW_{17}O_{61})_2]^{19-}$ derivatives, which were anticipated to be less susceptible to this type of crystallographic disorder than those containing XW_{18} or XW_{17}. This has proved to be the case.

Unlike the standard Wells−Dawson lacunary species α_2-$[X_2W_{17}O_{61}]^{10-}$, the $[H_4XW_{17}O_{61}]^{11-}$ precursors are metastable in aqueous solution, and it was necessary to add them as solid potassium salts to a solution of cerium(III) nitrate. The resulting complexes were isolated as the potassium salts, and crystals suitable for X-ray analysis were obtained as mixed ammonium−potassium salts.[15]

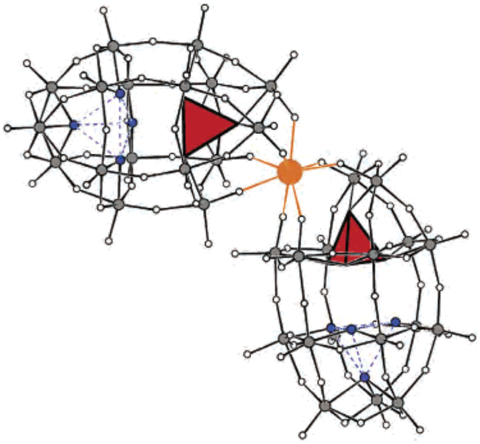

Figure 1. Ball-and-stick representation of the structure of **1**. Color scheme: gray, W; white, O; orange, Ce; blue, O(H) defining vacant tetrahedra; red, AsO_4 tetrahedra.

X-ray analysis[16] revealed the anticipated overall structure of C_2 symmetry for both anions and confirms that the tungsten vacancy is in the cap (α_2 position) at the phosphate end of the anion; see Figure 1. As for other $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{n-}$ (M = Ln, An) structures the polyoxometalate ligands adopt syn rather than anti conformations.[17] The structure of **2** shows a slight disorder of the three "cap" tungstens adjacent to the vacant tetrahedron, corresponding to a 60° rotation of that cap. This was modeled as the presence of a small proportion (10%) of the β isomer of the polyoxometalate ligand in the crystal examined. Although a similar set of three peaks was present in the final Fourier synthesis map of **1**, the intensities of these peaks were at the noise level for this structure ($\sim$2.5 $e^-/Å^3$), and attempts to model them as W atoms failed. The original report of the synthesis of $[H_4PW_{18}O_{62}]^{7-}$, from which the lacunary ver-

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(12) Fast proton exchange might be related to the fact that three of the oxygen atoms defining the vacant tetrahedron are only doubly bridging. In all other internally protonated polyoxotungstate structures that exhibit slower proton exchange, each of the oxygen atoms defining the vacant central O_4 tetrahedron is triply bridging and therefore more nucleophilic. (Note the localized protonation sites at triply bridging oxygens in the structure of $[H_2W_{12}O_{42}]^{10-}$: Evans, H. T., Jr.; Prince, E. *J. Am. Chem. Soc.* **1983**, *105*, 4838−4839).

(13) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737−2738

(14) Three hundred milligrams (59 μmol) of $K_7[H_4AsW_{18}O_{62}]\cdot18H_2O$ was dissolved in 1.00 mL of water, and the solution was added to 2.00 mL of C_6D_6 in which $[CH_3(CH_2)_6]_4NBr$ (0.15 g, 0.30 mmol) had been dissolved. The heterogeneous mixture was shaken for 10 min. Exactly 0.70 mL of the benzene layer was transferred to an NMR tube, 2.0 μL (25 μmol) of 1,2-dichloroethane ($C_2H_4Cl_2$) was added as an internal standard, and the 300-MHz ^1H NMR spectrum was recorded. The ratio of the integrated intensities of the 3.37-ppm ($C_2H_4Cl_2$) and 5.31-ppm ($[H_4AsW_{18}O_{62}]^{7-}$) signals was 1.8. The quantity (ca. 39 μmol) of $[H_4AsW_{18}O_{62}]^{7-}$ that had been transferred into the benzene layer was estimated by allowing the aqueous layer to evaporate and weighing the solid residue (110 mg). The NMR tube therefore contained $0.35 \times 39 = 13.6$ μmol of the polytungstate and 100 μmol of protons from dichloroethane. The number of protons contributed by each polytungstate anion is therefore $100/(1.8 \times 13.6) = 4.1$.

(15) To a solution of 0.22 g of cerium(III) nitrate hexahydrate (0.51 mmol) in 60 mL of warm (60 °C) deionized water was added 5 g of solid $K_{11}[H_4AsW_{17}O_{61}]\cdot18H_2O$ (1.01 mmol) in small portions. At first, the solution was cloudy and the H_4AsW_{17} did not dissolve completely, but after half the amount of H_4AsW_{17} was added, the solution cleared, and the remaining H_4AsW_{17} was added quickly. The deep orange solution was stirred for 30 min and was filtered while still warm. The product (anion **1**) was precipitated by adding 3 g of KCl to the warm solution. After filtration, the solid was recrystallized from the minimum amount of warm water (isolated yield 3.6 g, 72%). The tungstophosphate (anion **2**) was prepared analogously (yield 3.8 g, 76%). $K_{19}[Ce\{As(H_4)W_{17}O_{61}\}_2]\cdot21\cdot5H_2O$: Anal. Calcd (found): K, 7.71 (7.77); W, 64.87 (64.42); Ce, 1.45 (1.39). ^{183}W NMR: δ/ppm (integration) = +316.8 (2), +114.3 (2), −137.4 (2), −163.3 (1), −169.4 (2), −177.0 (2), −192.4 (2), −199.4 (2), −228.9 (2). $K_{19}[Ce\{P(H_4)W_{17}O_{61}\}_2]\cdot22H_2O$: Anal. Calcd (found): K, 7.78 (7.90); W, 65.47 (63.31); Ce, 1.47 (1.37). ^{183}W NMR: δ/ppm (integration) = +358.9 (2), +146.1 (2), −133.1 (2), −174.2 (2), −180.5 (2), −181.3 (1), −193.8 (2), −206.8 (2), −221.8 (2). ^{31}P NMR: −7.10 ppm. (Minor signals from isomers also observed; see ref 18.) Single crystals suitable for X-ray diffraction were grown by dissolving about 1 g of each salt in just enough warm water and adding 10−15 drops of saturated ammonium chloride solution. Orange crystals grew in less than 1 week as small needles.

(16) Crystallographic data. $(NH_4)_{11.5}K_{7.5}[Ce(As(H_4)W_{17}O_{61})_2]\cdot22H_2O$: Anal. Calcd (found): K, 3.11 (2.92); NH_4^+, 1.71 (1.45); formula weight, 9353.55; orthorhombic; space group, $P2_12_12$; $a = 43.335(9)$ Å; $b = 12.353(3)$ Å; $c = 14.795(3)$ Å; $V = 7920(3)$ Å^3; $Z = 2$; D(calcd) = 3.835 Mg m^{-3}; $\mu = 25.568$ mm^{-1}; $R(F_o^2) = 0.0589$; $R_w(F_o^2) = 0.1444$. $(NH_4)_9K_{10}[Ce(P(H_4)W_{17}O_{61})_2]\cdot19\cdot6H_2O$: Anal. Calcd (found): K, 4.20 (4.31); NH_4^+, 1.35 (1.24); formula weight, 9271.90; orthorhombic; space group, $P2_12_12$; $a = 43.477(16)$ Å; $b = 12.427(5)$ Å; $c = 14.861(6)$ Å; $V = 8029(5)$ Å^3; $Z = 2$; D(calcd) = 3.768 Mg m^{-3}; $\mu = 24.895$ mm^{-1}; $R(F_o^2) = 0.0711$; $R_w(F_o^2) = 0.1738$. Data were measured at 185 K on a Bruker-Siemens SMART CCD single-crystal diffractometer equipped with a Mo anode and graphite monochromator ($\lambda = 0.71703$ Å). An empirical absorption correction was used, based on measured intensities of equivalent reflections at different ϕ and ω values (Sheldrick, G. M. University of Gottingen, Gottingen, Germany, 1996. Blessing, R. *Acta Crystallogr. A* **1995**, *51*, 33). The structures were solved using direct methods and refined against $|F^2|$ over all independent reflections. SMART, SAINT, SHELX-97, and X-SEED software were used to solve and refine the data sets (Sheldrick, G. M. Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996, 1997. Barbour, L. J. 1999, http://x-seed.net/). As frequently seen in polyoxometalate structure determinations, there is extensive disorder of the cations and water molecules. To determine the occupancy of the disordered atoms, their atomic displacement parameter factors were first set to be comparable to those of the corresponding nondisordered atoms, and their occupancies were refined. Then, the occupancy numbers were held fixed, and the atomic displacement factors were refined.

(17) (a) Molchanov, V. N.; Kazanskii, L. P.; Torchenkova, E. A.; Simonov, V. I. *Sov. Phys. Crystallogr.* **1979**, *24*, 96. (b) Luo, Q.-H.; Howell, R. C.; Dankova, M.; Bartis, J.; Williams, C. W.; Horrocks, W. D., Jr.; Young, V. G.; Rheingold, A. L.; Francesconi, L. C.; Antonio, M. R. *Inorg. Chem.* **2001**, *40*, 1894−1901. (c) Ostuni, A.; Bachman, R. E.; Pope, M. T. *J. Cluster Sci.* **2003**, *14*, 431−446.

Table 1. Bond Valence Sum Data

anion	oxygens of vacant tetrahedra average (range)	all other bridging oxygens average (range)
1	1.10 (0.99−1.31)	1.99 (1.71−2.13)
2	1.09 (1.01−1.25)	1.95 (1.63−2.13)
α-$[(H_2)W_{12}O_{40}]^{6-}$ [a]	1.36 (1.16−1.37)	2.00 (1.88−2.08)

[a] In $[(CH_3)_4N]_6[(H_2)W_{12}O_{40}]\cdot 2H_2O$ (ref 21).

sions are derived, noted the presence of additional minor P NMR signals (tentatively attributed to *β* and *γ* isomers) that could be removed by prolonged boiling of the synthesis solution.[9,18]

Bond valence sums (BVSs) have proven to be reliable indicators of nondisordered protons in polyoxometalate structures.[19] BVS values[20] for all bridging oxygen atoms in both **1** and **2** provide strong evidence that each of the four internal oxygen atoms surrounding the "vacant" tetrahedra (shown in blue in Figure 1) is protonated. Relevant data together with those for the metatungstate anion[21] in which *two* protons are shared between the *four* internal oxygens are listed in Table 1.

The mean O···O distances spanning the edges of the vacant tetrahedron in**1** and the central tetrahedron in metatungstate are 2.91 and 2.88 Å, respectively (the corresponding distance for the AsO_4 tetrahedron in **1** is 2.72 Å). The question as to whether such tetrahedral cavities are large enough to accommodate as many as four protons seems to have been answered by the existence of the Himeno anion[8] mentioned above. It should be noted that, in the present case (anions **1** and **2**), as many as three of the internal OH vectors could be directed outside the vacant tetrahedron, i.e., into the adjacent trigonal prismatic cavity on the virtual equator of the W_{17} moiety.[12,22]

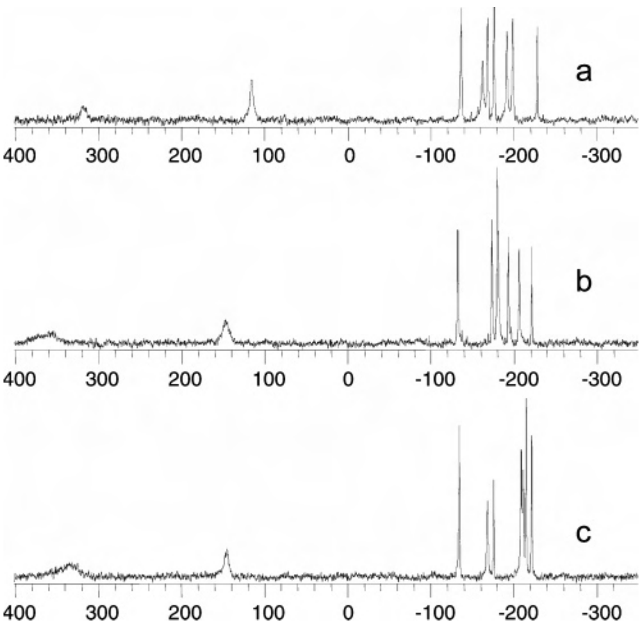

Figure 2. 12.505-MHz tungsten-183 NMR spectra of (a) **1**, (b) **2,** and for comparison (c) $[Ce(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$. Spectra were recorded on solutions of the lithium salts generated by treatment of the potassium salts with $LiClO_4$ solution.

Unlike the lacunary XW_{17} anions, the new 1:2 complexes are stable in aqueous solution and W NMR spectra of these solutions (Figure 2) are fully consistent with the C_2 symmetry observed in the crystal structures.

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Supporting Information Available: Crystallographic data for anions **1** and **2** in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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(18) The ^{31}P NMR spectrum of a solution of **2** showed, in addition to the main resonance at −7.10 ppm, a pair of lines at −8.78 and −16.90 ppm provisionally attributed to the complex with the (α, *β*) combination of ligands, as well as a weaker line at −18.66 ppm for the (*β*, *β*) species. The integrated intensities of the four lines indicated an average composition of 77% α and 23% *β* for that solution.

(19) See, for example, the discussion in: Dickman, M. H.; Ozeki, T.; Evans, H. T., Jr; Rong, C.; Jameson, G. B.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **2000**, 149−153.

(20) Brown, I. D.; Altermatt, D. *Acta Crystallogr. B,* **1985**, *41*, 244. A value of $R_0 = 2.120(14)$ was used to calculate the Ce−O bond valence sums ($b = 0.37$). This value is an improvement over those previously published and is valid for both Ce(III) and Ce(IV). It was derived from a series of low-temperature cerium(III) and cerium(IV) polyoxotungstate structures obtained at Georgetown University.

(21) Zavalij, P.; Guo, J.; Whittingham, M. S.; Jacobson, R. A.; Pecharsky, V.; Bucher, C. K.; Hwu, S.-J. *J. Solid State Chem* **1996**, *123*, 83−92.

(22) The corresponding cavity in $[Na(HOF_3)_2W_{18}O_{54}]^{7-}$ is occupied by the sodium cation (Jorris, T. L.; Kozik, M.; Baker, L. C. W. *Inorg. Chem.* **1990**, *29*, 4584−4586).