1.217 g cm^{-3}. The final R factor was 0.0461 ($Rw = 0.1328$) for 12902 reflections with $I > 2\sigma(I)$. Crystal data for **4a** · 0.5 C_6H_{14}: $C_{56}H_{105}Ge_3Si_3$, $M_r = 1080.47$, triclinic, space group = $P\bar{1}$, $a = 13.7810(7)$, $b = 14.485(1)$, $c = 15.339(1)$ Å, $\alpha = 100.917(3)$, $\beta = 91.953(4)$, $\gamma = 95.408(4)°$, $V = 2988.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.201$ g cm^{-3}. The final R factor was 0.0496 ($Rw = 0.1408$) for 10780 reflections with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144512 and CCDC-144513. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Direct Bromination of Keggin Fragments To Give $[PW_9O_{28}Br_6]^{3-}$: A Polyoxotungstate with a Hexabrominated Face**

R. John Errington,* Richard L. Wingad, William Clegg, and Mark R. J. Elsegood

The design and synthesis of polyoxometalates with specific structures and properties requires synthetic methodologies that enable framework morphology and surface functionality to be manipulated in a rational fashion and, although some progress has been made in recent years, there is still enormous scope for new, systematic chemistry in this area. Since the initial work by Knoth,[1] a particularly fruitful approach has been the attachment of organometal or organometalloid groups to lacunary species such as the tungstate Keggin fragments $[PW_{11}O_{39}]^{7-}$, $[SiW_{11}O_{39}]^{8-}$, $[SiW_{10}O_{36}]^{8-}$, $[PW_9O_{34}]^{9-}$, and $[SiW_9O_{34}]^{10-}$, and derivatives resulting from this strategy have been reviewed recently.[2] However, reactions involving the metathesis of labile halides, a ubiquitous method for ligand manipulation in synthetic organometallic and metal-organic chemistry, are not generally available for the surface functionalization of polyoxometalates because of the paucity of suitable halogenated derivatives. Although several fluoropolyoxoanions have been characterized,[2] and polyoxometalates containing heterometal–halide bonds have been prepared from reactions between lacunary anions and heterometal halides,[3] previously reported attempts to halogenate a polyoxometalate surface to produce reactive M–X sites resulted instead in degradation of the polyoxometalate framework and the production of low-nuclearity oxohalide complexes.[4] Herein we report the first successful halogenation of Keggin derivatives $[PW_9O_{34}]^{9-}$ and $[NaPW_{11}O_{39}]^{6-}$ and the structure of the resulting unique polyoxometalate with multiple terminal halide ligands.

The bromoanion $[PW_9O_{28}Br_6]^{3-}$ (**1**) was initially obtained as one of the products from the reaction between $(nBu_4N)_6$-$[NaPW_{11}O_{39}]$[5] and $C_2O_2Br_2$ in an attempt to attach oxalate groups to the surface of the PW_{11} Keggin fragment. The acetonitrile solvate of $(nBu_4N)_3$-**1** crystallized as yellow crystals along with colorless crystals of $(nBu_4N)_2[W_2O_4Br_4(\mu\text{-}C_2O_4)]$ and both compounds were structurally characterized by single-crystal X-ray diffraction.[6] The bromoanion **1** has the β,A-PW_9 structure (Figure 1), and is formally derived from the triply vacant lacunary Keggin anion β,A-$[PW_9O_{34}]^{9-}$ by replacement of six terminal oxo ligands with six bromo ligands, giving a molecular oxide with a fully brominated face. The structure of the dinuclear anion $[W_2O_4Br_4(\mu\text{-}C_2O_4)]^{2-}$ (**2**) is analogous to that of the molybdenum chloro analogue $[Mo_2O_4Cl_4(\mu\text{-}C_2O_4)]^{2-}$[7] and will be reported separately.

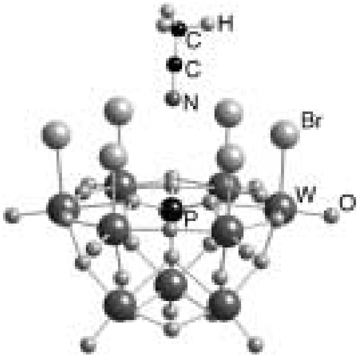

Figure 1. Structure of **1** showing also the position of the acetonitrile solvate molecule. Selected bond lengths [Å] and angles [°] (mean values within W_6 ring, values in parentheses are ranges of esds for individual measurements): W-Br 2.500(2–3), W-O_{term} 1.698(10–13), W-O(P) 2.399(10–11), W-O(W) (edge-sharing) 1.902(11–12), W-O(W) (corner-sharing) 1.881(10–12), W-O-W (edge-sharing) 125.3(5–6), W-O-W (corner-sharing) 159.9(6-7). Mean values between W_6 and W_3 rings: (Br)W-O(W) 1.875(11–13), (BrW)O-W 1.928(11–14), W-O-W 147.8(6).

The mean W–Br bond length of 2.50 Å in **1** is similar to that in **2** (2.52 Å) and, although no discrete β,A-$[PW_9O_{28}X_6]$ structures have previously been reported, W–O bond lengths in **1** are similar to those in α,A-$[PW_9O_{34}\{Si(tBu)OH\}_3]^{3-}$[8] and in $[(PhSnOH)_3(\beta\text{,A-}PW_9O_{34})_2]^{12-}$.[9]

Another feature of this crystal structure also shown in Figure 1 is the acetonitrile solvate molecule situated with the N atom 1.19 Å above the mean plane of the six bromo ligands, with N ··· Br distances of 3.773–4.053 Å. Partial occupancy of a second acetonitrile molecule position is correlated with disorder in some cation alkyl chains. The formation of **1** from $[NaPW_{11}O_{39}]^{6-}$ and $C_2O_2Br_2$ is consistent with a degradation process in which initial electrophilic attack at the basic oxide surface is followed by excision of two WO_2Br_2 fragments as the oxalato-bridged dinuclear complex **2**.

Bands for ν(P–O), ν(W=O), and ν(W-O-W) in the IR spectrum of $(nBu_4N)_3$-**1** are at higher wavenumbers than those for $Na_8H[PW_9O_{34}]$, as previously observed for α,A-$[PW_9O_{34}(RPO)_2]^{5-}$ ions.[10] A band at 928 cm^{-1} is low for terminal W=O, and may reflect stronger bonding in the

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asymmetric W-O-W bridges between the W_6 and W_3 rings due to the presence of *trans*-bromo ligands.

^{31}P and ^{183}W NMR spectra showed that **1** was produced in good yield from this reaction. The ^{31}P NMR peak for **1** occurs at $\delta_P = -11.6$, and in the ^{183}W NMR spectrum the brominated tungsten atoms WBr of **1** and WBr_2 of **2** have characteristic low-field chemical shifts with peaks at $\delta_W = 189.1$ and 281.6, respectively. The tungsten atoms in the W_3 cap of **1** give rise to a peak at $\delta_W = -123.1$, and the $^2J_{W,W}$ value of 25 Hz is consistent with previously reported values of $^2J_{W,W} > 10$ Hz for A-type EW_9 fragments.[8–11] The effect of bromination on δ_W can be seen by comparison with the ^{183}W NMR spectrum of $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$, the only other structurally characterized example of a functionalized polyoxometalate containing the β,A-PW_9 fragment.[9] In this "sandwich" anion, the tungsten atoms in the W_6 "belt" appear at $\delta_W = -202$, while the W_3 "cap" tungsten atoms appear at $\delta_W = -123$. Hence, replacement of terminal oxo by bromo ligands causes a downfield shift of about 390 ppm for the belt tungsten atoms, whereas δ_W for tungsten atoms in the W_3 cap is remarkably unaffected. This is consistent with the previously reported downfield shift of δ_W upon replacement of oxo by a chloro ligand,[4] although replacement of oxo by a fluoro ligand has been shown to result in an upfield shift.[12]

Bromination of $(nBu_4N)_6[NaPW_{11}O_{39}]$ with $SOBr_2$ also resulted in excision of two tungsten atoms and formation of $(nBu_4N)_3$-**1** as the major phosphotungstate product (67 % of the total integrated intensity in the ^{31}P NMR spectrum). In an effort to avoid framework degradation reactions and concomitant generation of tungsten oxobromide by-products, we treated $Na_8H[PW_9O_{34}] \cdot 23\,H_2O$[13] (after partial dehydration in vacuo at room temperature) with $SOBr_2$ in the presence of $(nBu_4N)Br$ and obtained 70–85 % yields of $(nBu_4N)_3$-**1**, as determined by ^{31}P NMR spectroscopy. Similar reactions were also carried out in the presence of the bases Et_3N and K_2CO_3 to minimize any structural rearrangements that might be caused by the presence of HBr generated from $SOBr_2$ and water of crystallization. In all cases **1** was formed in high yield, and the few phosphotungstate impurities present varied in number and amounts with the reaction conditions. The series of species β,A-$[PW_9O_{34-x}Br_x]^{(9-x)-}$ ($x = 0-6$) would give rise to seventeen ^{31}P NMR peaks (as would the α-isomeric series) and a much larger number of ^{183}W NMR peaks due the reduced symmetry of the partially brominated oxoanions. Bromination in the presence of K_2CO_3 appeared to be significantly cleaner by ^{31}P NMR spectroscopy (Figure 2), but samples of $(nBu_4N)_3$-**1** in this case were contaminated with small amounts of acetamide hemihydrobromide, $[(CH_3CONH_2)_2H]^+Br^-$, formed by hydrolysis of the MeCN solvent. Very few impurity peaks are observed in ^{183}W NMR spectra of $(nBu_4N)_3$-**1** samples, as shown in Figure 3, and the small peak at $\delta_W = -96.9$ can be assigned to $[PW_{12}O_{40}]^{3-}$.

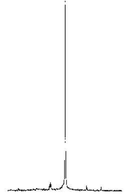

Figure 2. ^{31}P NMR spectrum (121.5 MHz, CH_3CN) of $(nBu_4N)_3$-**1** obtained by treatment of $Na_8H[PW_9O_{34}] \cdot 7\,H_2O$ with $SOBr_2$ and $(nBu_4N)Br$ in the presence of K_2CO_3.

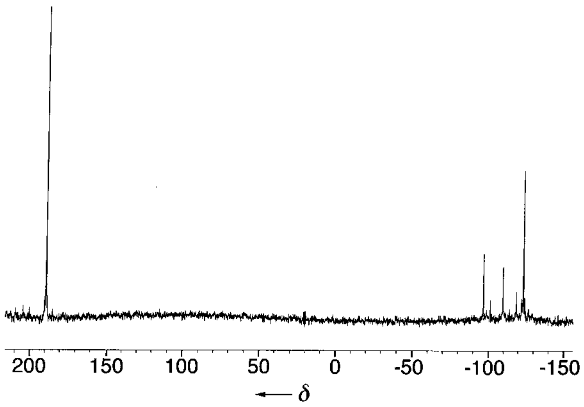

Figure 3. ^{183}W NMR spectrum (12.5 MHz, CH_3CN) of $(nBu_4N)_3$-**1** obtained by treatment of $Na_8H[PW_9O_{34}] \cdot 7\,H_2O$ with $SOBr_2$ and $(nBu_4N)Br$ in the presence of K_2CO_3.

Solutions of $(nBu_4N)_3$-**1** are stable in the absence of air, and the ^{31}P NMR spectrum of a sample in a screw-top NMR tube showed only a small amount of decomposition after one year at ambient conditions.

The reaction between $(nBu_4N)_3$-**1** and six equivalents of NaOMe has been monitored by ^{31}P NMR spectroscopy, and the number of peaks in the spectrum of the product suggested that the reaction had not gone to completion and that isomers of $[PW_9O_{28}Br_x(OMe)_{6-x}]$ were present. However, X-ray diffraction data on single crystals obtained from this reaction, although not of high quality, revealed a α,A-PW_9 structure,[14] demonstrating that structural rearrangement of the oxide framework occurs readily during metathesis of the bromo ligands in **1**.

In conclusion, we have achieved, for the first time, direct halogenation of polyoxometalate structures. The methodology used to prepare the hexabromoanion **1** from PW_9 or PW_{11} lacunary Keggin anions should be applicable to other polyoxometalates with basic surfaces, providing a range of halide derivatives for systematic studies of surface reactivity. Further studies on controlled halogenation of polyoxometalates, the optimization of reaction conditions and on the reactivity of **1** are in progress.

Experimental Section

All operations were carried out under dry dinitrogen using Schlenk and dry-box techniques.[15] Recrystallized $(nBu_4N)_3$-**1** was invariably contaminated with traces of other salts and consistent microanalytical results were not obtained.

$(nBu_4N)_3$-**1**: Method 1: A solution of $SOBr_2$ (0.37 mL, 4.68 mmol) in MeCN (10 mL) was added to a stirred mixture of $Na_8H[PW_9O_{34}] \cdot 7\,H_2O$ (2.00 g, 0.78 mmol) and nBu_4NBr (0.75 g, 2.34 mmol) in MeCN (20 mL) at −70 °C. The mixture was allowed to warm to room temperature and was then stirred overnight to give a yellow solution and a white precipitate. Volatiles were removed from the fitered solution and a yellow powder was obtained after trituration with diethyl ether (2.59 g).

Method 2: A solution of nBu$_4$NBr (7.85 g, 24.36 mmol) and SOBr$_2$ (8.3 mL, 105.56 mmol) in MeCN (10 mL) was added dropwise to a stirred suspension of Na$_8$H[PW$_9$O$_{34}$]$\cdot$7H$_2$O (20.81 g, 8.12 mmol) and K$_2$CO$_3$ (8.00 g, 57.88 mmol) in MeCN (200 mL) at −70 °C. After 1 h, the solution was filtered and the volatiles removed under reduced pressure. The resulting solid was redissolved in MeCN (40 mL) and filtered. Removal of the solvent and trituration with diethyl ether gave an orange powder (26.13 g). IR: $\tilde{\nu}$ = 1064 (s), 1022 (w), 998 (w), 989 (w), 974 (s), 928 (s), 868 (m), 787 (s, br), 737 (w), 580 (w), 519 (m) cm^{-1}.

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[6] Crystal data for (nBu$_4$N)$_3$-**1**$\cdot$1.56 MeCN: $C_{51.08}H_{112.62}Br_6N_{4.56}O_{28}PW_9$, $M_r = 3403.9$, monoclinic, space group $P2_1/n$, $a = 15.0129(10)$, $b = 25.831(2)$, $c = 22.8859(15)$ Å, $\beta = 93.452(2)°$, $V = 8859.0(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.552$ gcm^{-3}, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 14.43$ mm^{-1}, $T = 160$ K; of 37732 measured reflections corrected for absorption, 14773 were unique, $R_{int} = 0.0668$; $R = 0.0600$ ($I > 2\sigma$), $R_w = 0.1345$ (F^2, all data), GOF = 1.147, 968 parameters, final difference map extremes +2.38 and −1.20 e Å^{-3}. Disorder was refined for some alkyl chains and one partially occupied acetonitrile position with the aid of restraints. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139046. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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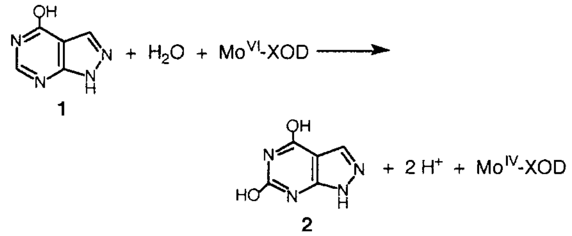
Control of Xanthine Oxidase Activity by Light[**]

Lin Ai Tai and Kuo Chu Hwang[*]

Photocontrol of enzyme activities has been a subject of active research.[1–8] Natural photoenzymes are very rare. To date, only three natural photoenzymes have been reported, namely, DNA photolyase,[9] [6–4] photoproduct lyase,[10] and protochlorophyllide reductase.[11] With their ability of transforming optical signals into chemical motion, photoenzymes might have important future applications in molecular-scale electronics in the areas of signal transformation, amplification, integration, and information storage.

Previously, photoinduced release of a light-active antigen from an antibody was reported.[12] Photochemical inhibition of nicotinic acetylcholine receptors by a photoisomerizable inhibitor was also reported.[13] Enzymes can also be chemically modified by covalently bonding a “gating molecule” to the neighborhood of the enzyme active site[3–5] or at the enzyme cofactor[6–8] to control the entry of substrates. Common gating molecules of choice are photoisomerizable olefins and photochromic compounds. Chemical modification of natural enzymes often results in partial loss of enzyme activity. Moreover, the location of the gating molecule is limited to the availability of chemically modifiable amino acids around the active site, and is quite difficult to control at will. Herein, we report a simple, novel xanthine oxidase (XOD) photoenzyme system, with allopurinol as a substrate, in which the activity can be switched on or off by light. A photoinduced intra-enzyme electron-transfer model is proposed to rationalize the photoregulation of XOD activity.

XOD is a 300 kDa homodimer protein, with each unit containing a molybdenum(VI), two Fe/S clusters, and one flavin adenine dinucleotide (FAD) moiety.[14] The Mo^{VI} ion at the active site can activate a water molecule and oxidize a C–H bond in various substrates to C–OH. After gaining two electrons from the substrate, Mo^{IV} passes two electrons sequentially, by way of the Fe/S clusters, to the FAD cofactor which then reduces molecular oxygen to generate superoxide (or hydrogen peroxide in acidic conditions).[15] As an XOD substrate, allopurinol (**1**) is oxidized and converted to alloxanthine (**2**) [Equation (1)], which is a potent, slow-



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