



Supporting Information

© Wiley-VCH 2007

69451 Weinheim, Germany

Multiple Reversible Protonation of Polyoxoanion Surfaces: Direct Observation of Dynamic Structural Effects from Proton Transfer

Xikui Fang and Craig L. Hill*

Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322

Characterization data for 1 and 2

1: ^{31}P NMR (6 mM, referenced to 85% H_3PO_4): $\delta = -7.09$ and -12.36 ppm; IR (KBr, cm^{-1}): $\tilde{\nu} = 1087(\text{s}), 1053(\text{sh}), 1017(\text{sh}), 944(\text{s}), 915(\text{s}), 822(\text{sh}), 755(\text{s}), 523(\text{m})$. Elemental analysis: Calcd Zr, 1.08; P, 1.46; W, 65.18; C, 3.41; H, 1.74; N, 1.99. Na, 0. Found Zr, 1.18; P, 1.49; W, 63.55; C, 3.33; H, 1.61; N, 2.06. Na, < 0.1 . The number of water molecules of crystallization was determined by thermogravimetric analysis (TGA). Both elemental analysis data and ^{13}C NMR integration results (by addition of a known amount of $\text{CH}_3)_2\text{NH}_2\text{Cl}$ indicated that all countercations are dimethylammonium (no Na^+ or H^+ counterions are present).

2: ^{31}P NMR (6 mM, referenced to 85% H_3PO_4): $\delta = -6.38, -9.19, -12.21$ and -13.41 ppm; IR (KBr, cm^{-1}): $\tilde{\nu} = 1085(\text{s}), 1019(\text{w}), 946(\text{s}), 922(\text{sh}), 896(\text{sh}), 784(\text{s}), 749(\text{sh}), 525(\text{m})$. Elemental analysis: Calcd Zr, 1.00; P, 1.36; W, 64.61; C, 3.69; H, 1.88; N, 2.15. Na, 0. Found Zr, 1.08; P, 1.46; W, 66.13; C, 3.84; H, 1.93; N, 2.32. Na, < 0.1 . The numbers of hydration water and counterions were determined with the same techniques used for **1**.

Details of Single Crystal X-ray Structure Analyses

Suitable crystals were coated with Paratone N oil, suspended on a small fiber loop, and placed in a cooled nitrogen stream at 173 K on a Bruker D8 SMART APEX CCD sealed-tube diffractometer with graphite-monochromated Mo K α (0.71073 Å) radiation. A sphere of data was measured using a series of combinations of ϕ and ω scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinements were all handled using SMART software.^[1] Frame integration and final cell refinements were carried out using SAINT software.^[2] The final cell parameters were determined from least-squares refinement on 56372 and 25554 reflections for **1** and **2**, respectively. The SADABS program was used to carry out absorption corrections.^[3] The structure was solved using Direct Methods and difference Fourier techniques (SHELXTL, V6.12).^[4] All metal atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.^[5] Structure solution, refinement and generation of publication materials were performed by using SHELXTL, V6.12 software.^[4] Only the heavy atoms (W and Zr) were refined anisotropically. The hydrogen atoms on the counterion were included at idealized positions and were allowed to ride on the atom to which they are bonded. In both **1** and **2**, not all of the cationic counterions and the lattice water molecules could be located due, in part, to disorder. Also due to the disorder problems, some the oxygen atoms for the solvent water molecules were assigned with partial occupancies. Therefore, the missing water molecules and disordered counteractions that cannot be located in the Fourier difference map were added to the formula in the final cycles of refinement. Associated changes in formula weight, density, μ and $F000$ were accordingly made in the refinement, and this can explain the difference in calculated values and reported ones.

Complex **1** crystallizes in an asymmetric space group $P1$, with two molecules per unit cell. Efforts to solve the structure assuming the alternative achiral space group $P-1$ failed, although the heavy atom frameworks of the two molecules appear to be approximately centrosymmetric to each other. This is likely due to the packing of $(\text{CH}_3)_2\text{NH}_2^+$ counteractions and/or solvent molecules, which can reduce the symmetry of the crystal. Solving the structure of **2** using direct methods and difference Fourier techniques was quite straightforward, but the actual refinement suggests that a

rotational disorder of the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ unit with respect to the hinge Zr atom occurs. The disorder model (see the next section) refines satisfactorily with two equally-weighted parts for the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ unit, with one rotated by *ca.* 6° relative to the other.

Disorder modeling in the crystal structure analysis of 2

While the polyanion in the X-ray structure of **1** was disorder free, the polyanion in the X-ray structure of **2** exhibited an interesting minor rotational disorder. The structure solution of **2** using direct methods and difference Fourier techniques was quite straightforward (Figure S1). However, the refinement encountered some problems with the model shown in Figure S1 (left). First, many oxygen atoms, especially those in the lower part of the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ unit had surprisingly large temperature factors relative to the others (not shown in the figure for clarity). Second, some of the anisotropically refined W atoms have anomalous elongated ellipsoids (e.g. W30, W31 and W32), and the associated effect of this is large electron residues (up to $9 \text{ e } \text{\AA}^{-3}$) close to those heavy atoms. These strangely anisotropic ellipsoids of W atoms cannot be explained by unsatisfactory absorption correction since such corrections apply homogeneously throughout the unit cell. Thermal ellipsoid elongation only takes place in the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ moiety, not the $\text{P}_2\text{W}_{15}\text{O}_{56}^{12-}$ moiety, and becomes more prominent on going down to the lower terminus of the structure. This strongly suggests that a slight rotational disorder of the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ unit with respect to the hinge Zr atom is operable. In practice, refinement using such a rotational-disorder model was quite time-consuming because the disorder involves about 80 atoms and one must assume the disordered parts have similar connectivities between the atoms in order to achieve refinement convergence. The disorder model (Figure S1, right) refines satisfactorily with two equally-weighted parts for the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ unit, with one rotated by *ca.* 6° relative to the other. The two parts only share the same Zr hinge, and the rotation is such that the splitting between them is more severe near the lower terminus of the structure than in the area close to the Zr atom. This explains the anomalously anisotropic ellipsoids for W and large temperature factors for isotropically refined O atoms when using a non-disordered model. As seen in Figure S1 (right), the heavy atom frameworks of the two orientations now behave normally and so do the sets of oxygen and the P atoms. The highest electron residue in the difference maps is reduced to $3.6 \text{ e } \text{\AA}^{-3}$.

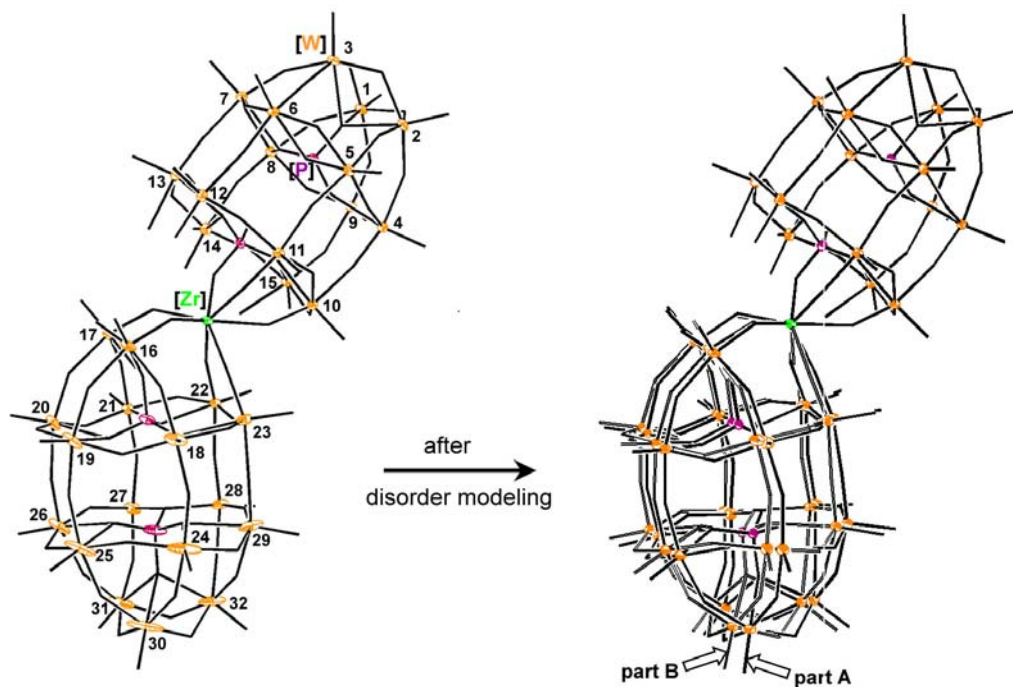


Figure S1. Disorder modeling in the crystal structure analysis of **2**

References

- [1] SMART Version 5.628, **2003**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- [2] SAINT Version 6.36A, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- [3] SADABS Version 2.08, **2003**, George Sheldrick, University of Göttingen.
- [4] SHELXTL 6.12, **2002**, Bruker AXS, Inc., Analytical X-ray Systems, 5465 East Cheryl Parkway, Madison WI 53711-5373.
- [5] A. J. C. Wilson (ed), International Tables for X-ray Crystallography, Volume C. Kynoch, Academic Publishers, Dordrecht, **1992**, Tables 6.61.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222).