Crystal Structure Analysis of a Hexatungstate by a High-Energy X-ray Diffraction Experiment Using an Imaging Plate Weissenberg Camera at the BL04B2 Beamline of SPring-8[1]

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An imaging plate Weissenberg camera was installed in the BL04B2 beamline of SPring-8 aiming at automated crystal structure determinations of small molecules. Since this beamline is designed to provide X-rays with the energies higher than 37 keV ($\lambda < 0.33$ Å), this camera is advantageous in crystal structure analyses of heavily X-ray absorbing materials. The title crystal structure analysis led to precise positional parameters and well-behaved displacement parameters not only for heavy atoms but also for light atoms.

Synchrotron radiation (SR) has made an enormous impact to crystallography since its discovery.[2,3] However, apart from biological macromolecules, advantages of the use of SR have not been fully exploited for the single crystal structure determination, which is undoubtedly the most popular contribution of crystallography to chemistry. Only a handful of facilities have been utilized for determining crystal structures of small molecules of chemical interest.[4] Moreover, there are only a few facilities that are entirely devoted for chemical crystallography.[5] Modern SR facilities storing higher energy electron beams (typically higher than 6 GeV) such as SPring-8 have an advantage of providing high-energy X-rays (wavelengths much shorter than Mo Kα radiation) at sufficient flux. Diffraction experiments using high-energy X-rays suffer less absorption and extinction and are thus expected to provide results free from systematic errors caused by these effects. Although exploitations of the advantages of using high-energy SR for X-ray diffraction experiments had been limited to charge-density[6] and diffuse scattering[7] studies, our previous report demonstrated that reduction of the effect of absorption by using high-energy SR X-ray enabled a structure determination of a heavy metal polynuclear compound with high precision.[8] In these contexts, we have installed an automated imaging plate Weissenberg camera into the BL04B2 beamline of SPring-8, as a facility purely dedicated to crystal structure determinations of non-biological small molecules. As the BL04B2 beamline is designed to provide a high-energy X-ray beam,[9] this instrument is expected to be powerful in determining the structures of highly X-ray absorbing crystals.

A DIP-Labo diffractometer, an automated imaging plate (IP) Weissenberg camera from MAC Science Co., Ltd., was installed in the BL04B2 beamline of SPring-8. It utilizes 37.78 keV (0.3282 Å) X-ray monochromated by a Si(111) crystal. It is equipped with an imaging plate with the size of 240 × 420 mm that is made cylindrical with a radius of 120 mm around the ω axis of a κ-type three-circle goniometer. After exposure, the diffraction image recorded on the IP is automatically processed by an integrated IP reader. A shutter, a collimating system and a beam-stop were modified, which can be seen in Figure 1.[10]

As an example of heavily X-ray absorbing materials, bis(tetrabutylammonium) hexatungstate[11] was employed. It is a polyoxotungstate containing six W atoms. Single crystals were obtained by recrystallizing crude product from acetone. The crystal used in this experiment measured 0.097 × 0.064 × 0.020 mm, which would cause severe absorption for MoKα radiation (μ for Mo Kα is 14.3 mm^{-1}). However, 37.78 keV X-ray suffers negligible amount of absorption by a crystal of this size, even though it contains a large number of heavy elements (μ for 37.78 keV is 1.91 mm^{-1}). A total of 59 diffraction images were automatically collected on an imaging plate and were indexed and integrated using the program DENZO.[12] Intensity data were corrected for Lorentz and polarization but not for absorption effects. The structure was solved by analyzing a three-dimensional Patterson synthesis and refined by full-matrix least squares on F^2 using SHELXL-97.[13] Anomalous scattering factors and X-ray absorption coefficients were taken from References 14 and 15, respectively. Summary of the experimental conditions and crystal data are listed in Table 1.

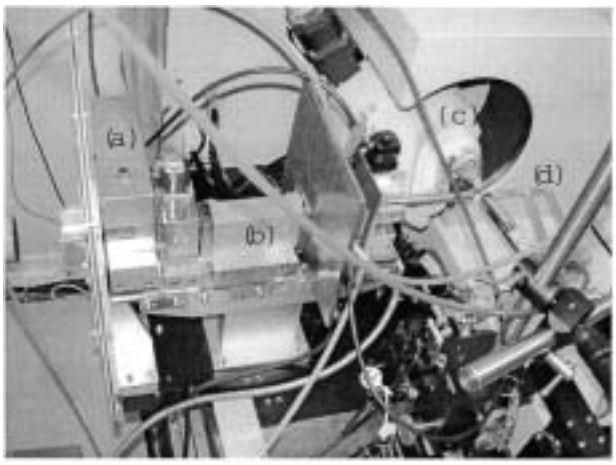

Figure 1. A perspective view of the imaging plate Weissenberg camera installed in the BL04B2 beamline of SPring-8: (a) high-speed shutter, (b) collimating system, (c) κ-type three-circle goniometer, and (d) adjustable beam-stop.

Table 1. Summary of experimental conditions and crystal data

Chemical formula	$C_{32}H_{72}N_2W_6O_{19}$
Formula weight	1892.0
Space group	$P\bar{1}$
Z	2
a / Å	11.671(1)
b / Å	12.649(1)
c / Å	19.191(1)
α / °	78.78(1)
β / °	74.48(1)
γ / °	62.61(1)
Wavelength / Å	0.3282
μ (37.78 keV) / mm^{-1}	1.91
μ (Mo Kα) / mm^{-1}	14.3
Temperature / K	130
Data collection mode	Oscillation method
Oscillation width per frame / °	4
Scan speed / ° min^{-1}	3
(sin θ / λ)$_{max}$ / Å^{-1}	0.909
Total number of data collected	46399
R_{int}	0.0445
Completeness / %	88.8
Number of independent data	26928
Number of parameters	544
$R(F)$ ($F_o > 4\sigma(F_o)$)	0.0357
$wR(F^2)$ (all reflections)	0.0767
$\Delta\rho_{max}$ / eÅ^{-3}	2.20
$\Delta\rho_{min}$ / eÅ^{-3}	-1.85

Obtained data were of sufficient quality to give a well-resolved three-dimensional Patterson map to warrant a straightforward solution. The obtained crystal structure is basically identical with those already reported,[11] except for that the current analysis revealed a disorder of one of the terminal ethyl groups of a tetrabutylammonium cation over two sites with the occupancies of 0.88(1) and 0.12(1). ORTEP[16] diagrams of the $[W_6O_{19}]^{2-}$ anions are shown in Figure 2. Although no absorption corrections were applied, the least-squares refinements were successfully converged without any systematic distortions. It is noteworthy that all the non-hydrogen atoms in the crystal, except for the less occupied part of the disordered group, were stably refined using anisotropic displacement parameters. In many polyoxotungstate crystals, only heavy atoms can be refined anisotropically and anisotropic refinements of lighter atoms tend to result in non-positive definite or extremely skewed displacement parameters. However, there are no unrealistically distorted displacement ellipsoids, as shown in Figure 2. Also, the positional parameters of lighter atoms were refined to give sufficient precision, which is illustrated by small standard uncertainties associated with the W–O distances shown in Figure 2.

As is demonstrated here, the imaging plate Weissenberg camera installed in the BL04B2 beamline of SPring-8 was proved to be powerful in structure determinations of heavy metal polynuclear compounds with high precision. Detailed interpretations of geometries involving lighter atoms become possible even without any corrections for the effect of absorption. Most of the inconveniences encountered in our previous experiment[8] were overcome.

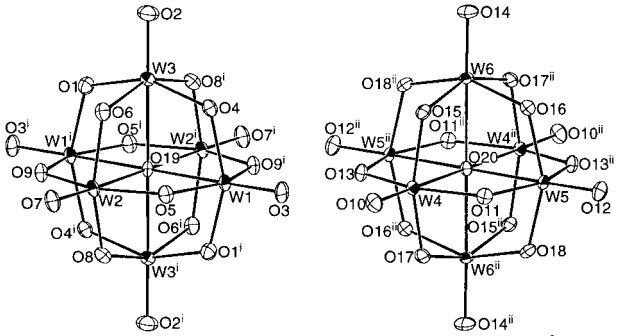

Figure 2. ORTEP drawings of the two independent $[W_6O_{19}]^{2-}$ anions. Displacement ellipsoids are scaled to enclose 50% probability levels. Selected distances (Å): W1-O3 1.717(3), W1-O9^{i} 1.927(3), W1-O1^{i} 1.928(3), W1-O4 1.936(3), W1-O5 1.946(3), W1-O19 2.332(1), W2-O7 1.716(3), W2-O8 1.916(3), W2-O5 1.927(3), W2-O9 1.943(3), W2-O6 1.955(3), W2-O19 2.339(1), W3-O2 1.712(3), W3-O6 1.923(3), W3-O4 1.931(3), W3-O1 1.938(3), W3-O8^{i} 1.960(3), W3-O19 2.351(1), W4-O10 1.718(3), W4-O15 1.929(3), W4-O11 1.929(3), W4-O13 1.940(3), W4-O17 1.942(3), W4-O20 2.338(1), W5-O12 1.717(3), W5-O16 1.925(3), W5-O13^{ii} 1.933(3), W5-O18 1.935(3), W5-O11 1.950(3), W5-O20 2.344(1), W6-O14 1.718(3), W6-O15 1.935(3), W6-O18^{ii} 1.935(3), W6-O16 1.936(3), W6-O17^{ii} 1.940(3), W6-O20 2.340(1). Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, 1-z$.

The synchrotron radiation experiment was performed at SPring-8 BL04B2 beamline under an agreement with JASRI. Purchasing the diffractometer was supported by JST and its installation to SPring-8 was supported by JST and JASRI.

References and Notes

1 High-Energy X-ray Structure Determinations Using Synchrotron Radiation. Part 2. Part 1: Reference 8.
2 P. Coppens, "Synchrotron Radiation Crystallography," Academic Press, London (1992).
3 J. R. Helliwell, *Acta Crystallogr., Sect. A*, **54**, 738 (1998).
4 W. Clegg, *J. Chem. Soc., Dalton Trans.*, **2000**, 3223 and references therein; Y. Cerenius, K. Ståhl, L. A. Svensson, T. Ursby, Å. Oskarsson, J. Albertsson, and A. Liljas, *J. Synchrotron Rad.*, **7**, 203 (2000).
5 R. J. Cernik, W. Clegg, C. R. A. Catlaw, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, I. Burrows, D. J. Taylor, S. J. Teat, and M. Hamachi, *J. Synchrtron Rad.*, **4**, 279 (1997).
6 H. Graafsma, S. O. Svensson, and A. Kvick, *J. Appl. Crystallogr.*, **30**, 957 (1997); T. Koritsanszky, R. Flaig, D. Zobel, H. G. Krane, W. Morgenroth, and P. Luger, *Science*, **279**, 356 (1998); P. Coppens, *Acta Crystallogr., Sect. A*, **54**, 779 (1998); R. Flaig, T. Loritsanszky, J. Janczak, H. G. Krane, W. Morgenroth, and P. Luger, *Angew. Chem. Int. Ed.*, **38**, 1397 (1999); P. Coppens, Y. Abramov, M. Carducci, B. Korjov, I. Novozhilova, C. Alhambra, and M. R. Pressprich, *J. Am. Chem. Soc.*, **121**, 2585 (1999); P. R. Mallinson, G. Barr, S. J. Coles, T. N. Guru Row, D. D. MacNicol, S. J. Teat, and K. Wozniak, *J. Synchrotron Rad.*, **7**, 160 (2000).
7 B. D. Butler, D. R. Haeffner, P. L. Lee, and T. R. Welberry, *J. Appl. Crystallogr.*, **33**, 1046 (2000).
8 T. Ozeki, *Chem. Lett.*, **2001**, 266.
9 M. Isshiki, Y. Ohishi, S. Goto, K. Takeshita, and T. Ishikawa, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **467–8**, 663 (2001).
10 A detailed description of the instrument will be published elsewhere.
11 J. Fuchs, W. Freiwald, and H. Hartl, *Acta Crystallogr., Sect. B*, **34**, 1764 (1978).
12 Z. Otwinowski and W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode," in "Methods in Enzymology," ed. by C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York (1997), Vol. 276, Part A, p 307.
13 G. M. Sheldrick, SHELX-97, Program for the Analysis of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
14 S. Sasaki, *KEK Report*, **88-14**, 1 (1989).
15 M. J. Berger, J. H. Hubbell, S. M. Seltzer, J. S. Coursey, and D. S. Zucker, XCOM: Photon Cross Section Database (version 1.2). Available: http://physics.nist.gov/xcom. National Institute of Standards and Technology, Gaithersburg, MD, U.S.A., 1999.
16 M. N. Burnett and C. K. Johnson, ORTEP-III, ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A., 1996.