Structure Analysis of a Sodium Paradodecatungstate[1]

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The crystal structure of a sodium paradodecatungstate has been analyzed using high-energy X-rays at the SPring-8 BL02B1 beamline, aiming at an absorption free structure determination of polynuclear heavy metal compounds. Effect of the use of high-energy synchrotron radiation has been demonstrated and the result was of sufficient quality

One of the most serious problems encountered when analyzing the crystal structures of compounds containing heavy elements by X-ray diffraction is the absorption effect that introduces a systematic error to measured diffraction intensities. Although absorption corrections can be applied using various methods,[2] they are in many cases of limited accuracy, especially when it is difficult to make accurate measurements of the crystal shape and size due to the crystals not having well-developed faces or being sealed in capillaries. Diffraction data not or insufficiently corrected for the effect of absorption lead to unrealistically distorted anisotropic displacement parameters and poor fit between observed and calculated structure factors. The latter particularly decreases the precision of positional (and displacement) parameters of lighter atoms, which accordingly makes geometric parameters involving these atoms less reliable. A much better way to avoid this systematic error is, without any doubt, to diminish the absorption effect, which can be achieved either by making the crystal size smaller or by reducing the absorption coefficients of the material under study. The former is not practical because crystals should be large enough for the diffraction to be observed with sufficient signal to noise ratio. The latter can be realized when using high-energy, or short wavelength, X-rays. However, conventional sources (sealed tubes or rotating anodes) cannot generate X-rays with sufficient intensity at wavelengths shorter than MoKα radiation. In the past decade, third generation synchrotron storage rings that generate high-energy X-rays with sufficient brilliance became available, the exploitation of which should solve the aforementioned difficulties. Recently, a seven-circle goniometer was installed in the BL02B1 beamline of SPring-8.[3] It is equipped with an imaging-plate cylindrical vacuum camera that enables single crystal structure analyses.[3] An attempt to carry out a structure analysis of heavy metal compounds with high-energy X-rays using this apparatus was initiated and its result is reported here.

As an example of heavily X-ray absorbing materials, sodium paradodecatungstate 26-27 hydrate[4] was employed. It is a polyoxotungstate containing 12 W atoms, whose linear absorption coefficient is as large as 23.2 mm^{-1} for MoKα radiation. Single crystals were obtained by slowly evaporating its concentrated aqueous solutions. To avoid efflorescence under vacuum, a crystal with the dimension of 0.2 × 0.2 × 0.1 mm was sealed in a glass capillary and mounted on the Huber seven-circle goniometer at the BL02B1 beamline of SPring-8. Diffraction data were collected on imaging plates using the vacuum camera attached to the diffractometer. Diffraction images recorded on imaging plates were indexed and integrated using the program DENZO.[5] Intensity data were corrected for Lorentz and polarization but not for absorption effects. The structure was solved by direct methods using SHELXS-97[6] and refined by full-matrix least-squares on F^2 using SHELXL-97.[6] Anomalous scattering factors and X-ray absorption coefficients were taken from References 7 and 8, respectively. Summary of the experimental conditions and crystal data are listed in Table 1.[9]

Table 1. Summary of experimental conditions and crystal data

Chemical formula	$Na_{10}H_2W_{12}O_{42}\cdot 26H_2O$
Formula weight	3578.8
Space group	$P\bar{1}$
Z	2
a / Å	11.881(1)
b / Å	12.557(1)
c / Å	22.319(3)
α / °	86.214(4)
β / °	86.163(5)
γ / °	66.249(5)
Wavelength / Å	0.3937
μ (30.748 keV) / mm^{-1}	5.28
μ (Mo Kα) / mm^{-1}	23.2
Data collection mode	Oscillation method
Oscillation width per frame / °	6
Overlap between each frame / °	1
Scan speed / ° min^{-1}	0.25
$(\sin\theta/\lambda)_{max}$ / $Å^{-1}$	0.893
Total number of data collected	30843
R_{int}	0.0710
Completeness / %	54.8
Number of independent data	19516
Number of parameters	812
$R(F)$ ($F_o>4\sigma(F_o)$)	0.0444
$wR(F^2)$ (all reflections)	0.1182
$\Delta\rho_{max}$ / $eÅ^{-3}$	2.54
$\Delta\rho_{min}$ / $eÅ^{-3}$	-2.57

Obtained data were of sufficient quality to warrant a successful structure solution by direct methods without any special treatments. The obtained crystal structure is identical with those already reported[10,11] within experimental errors, except for some disordered water molecules of crystallization. An ORTEP[12] diagram of the $[H_2W_{12}O_{42}]^{10-}$ anion is shown in Figure 1. Although no absorption corrections were applied and only 54.8% of the independent reciprocal space below $\sin\theta/\lambda$ of 0.893 $Å^{-1}$ was measured, the least-squares refinements were

successfully converged without any systematic distortions. No restraints or constraints were necessary except for the occupancy factors for the disordered atoms. It is noteworthy that all the O atoms in the crystal, except for those disordered, were stably refined using anisotropic displacement parameters. In many polyoxotungstate crystals, only heavy atoms can be refined anisotropically and anisotropic refinements of O atoms tend to result in non-positive definite or extremely skewed displacement parameters. However, there is no unrealistically distorted displacement ellipsoid, as shown in Figure 1. Also, the positional parameters of O atoms were refined to give sufficient precision. Standard uncertainties for the geometric parameters involving O atoms are considerably small: 0.004–0.007 Å [average 0.006 Å] for W–O distances, 0.2–0.3° [average 0.2°] for O–W–O angles, and 0.2–0.4° [average 0.3°] for W–O–W angles.

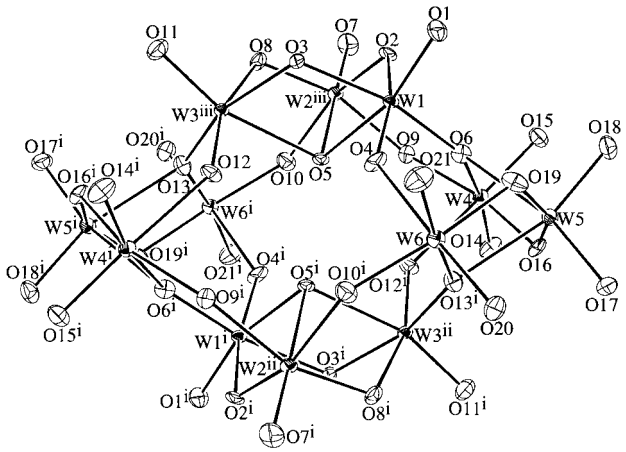

Figure 1. An ORTEP drawing of one of the two independent $[H_2W_{12}O_{42}]^{10-}$ anions. Displacement ellipsoids are scaled to enclose 50 % probability levels. Numbering scheme follows Reference 11. Symmetry codes: (i) 1-*x*, 1-*y*, -*z*; (ii) *x*, *y*, -1+*z*; (iii) 1-*x*, 1-*y*, 1-*z*.

As is demonstrated here, reduction of the effect of absorption by using high-energy synchrotron X-ray radiation enables 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. However, there are some experimental inconveniences: (a) imaging plates should be manually set to the camera and the reader, (b) only rotation around one axis is allowed and data collections with higher completeness and redundancy are impossible, (c) data should be collected at room temperature, (d) relatively long exposure time is needed. Currently, a new experimental station is under development to overcome these inconveniences.[13]

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References and Notes

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