

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1261). Services for accessing these data are described at the back of the journal.

## References

- Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1998). *Inorg. Chem.* **37**, 5941–5943.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hester, C. A., Baughman, R. G. & Collier, H. L. (1997). *Polyhedron*, **16**, 2893–2895.
- Kasselouri, S., Garoufis, A., Kathanakis, A., Kalkanis, G., Perlepos, S. P. & Hadjiladis, N. (1993). *Inorg. Chim. Acta*, **207**, 255–258.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Psillakis, E., Jeffery, J. C., McCleverty, J. A. & Ward, M. D. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1645–1651.
- Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tong, M. L., Chen, X. M., Ye, B. H. & Ng, S. W. (1998). *Inorg. Chem.* **37**, 5278–5281.

*Acta Cryst.* (1999). **C55**, 2037–2039

## Dioxobis(8-quinolinolato-*N,O*)tungsten(VI)

S. SHANMUGA SUNDARA RAJ,<sup>a</sup> HOONG-KUN FUN,<sup>a</sup>  
ZHEN-FENG CHEN,<sup>b</sup> JING ZHANG,<sup>b</sup> XIANG XUE,<sup>b</sup>  
REN-GEN XIONG<sup>b</sup> AND XIAO-ZENG YOU<sup>b</sup>

<sup>a</sup>*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and*

<sup>b</sup>*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China. E-mail: hkfun@usm.my*

(Received 13 July 1999; accepted 5 August 1999)

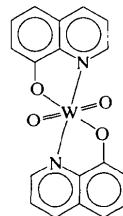
## Abstract

The crystal structure of the title complex, [WO<sub>2</sub>(C<sub>9</sub>H<sub>6</sub>NO)<sub>2</sub>], a hexacoordinated molecule, has distorted octa-

hedral geometry with C<sub>2</sub> site symmetry. There are two terminal O ligands with a short W—O bond length [1.722(4) Å] and a large O—W—O angle [106.6(3)°] in the molecule. The two terminal O ligands are in *cis* positions. The molecules join to form a two-dimensional network parallel to (001) through C—H···O hydrogen bonds.

## Comment

8-Quinolinol has been used widely to determine the quantity of tungsten and molybdenum (Marcel & Rene, 1950). The complexes of 8-quinolinol with niobium, molybdenum, tungsten and hafnium emit interesting fluorescence (Schneider & Roselli, 1970). Photocatalyzed synthesis, characterization and thermal behavior of tungsten(IV) complexes with oxine has been studied (Ali & Yunhir, 1993). Although dioxotungsten complexes with oxine were prepared by various methods, so far, the hydrothermal treatment of carbonyl tungsten, 8-quinolinol and methanol has not been reported. Moreover, the crystal structure of the title compound, (I), to the best of our knowledge, has not been reported previously.



(I)

The bond angles in the aromatic ring system are found to be between 118.2(5) and 121.7(5)°. In the 8-quinolinolato ligands, the absence of any unusually long bonds and the marginally longer carbonyl bond [1.355(6) Å versus 1.28 Å], shorter than the normal single bond in ether and alcohols (>1.4 Å), suggest that the delocalization extends over the entire molecule and will therefore withdraw more negative charge from the cation (Barton *et al.*, 1983).

The two bidentate ligands are arranged at an angle of 83.2(1)° with respect to one another in a *cis* geometry, and the W atom therefore represents a center of chirality. The *cis* topology is in agreement with several examples of hexacoordinate complexes with bidentate ligands like *o*-phenanthroline, bipyridine or 8-quinoline (Sawitzki *et al.*, 1978; Bellavance *et al.*, 1977; Klebe & Tran Qui, 1984), and can be explained in stereochemical terms: the *cis* geometry of the ligands minimizes the steric interference between the H atoms in the 2 and 4 positions of the different ring systems. In the title complex, the chelate ligands are connected to the central W atom through a W—O single bond and a W—N coordinative bond. The two W—O (O2) bonds form

an angle of 150.9(2)° and the N—W—N<sup>i</sup> angle is 76.9(2)° [symmetry code: (i)  $-x, y, \frac{1}{2} - z$ ]. The O1—W—O1<sup>i</sup> angle [106.6(3)°] is slightly larger than that in [MoO<sub>2</sub>(C<sub>9</sub>H<sub>6</sub>NO)<sub>2</sub>] [105.9(3)°]. The W—O bond length of 1.722(4) Å is similar to the Mo—O distance [1.714(5) Å] in [MoO<sub>2</sub>(C<sub>9</sub>H<sub>6</sub>NO)<sub>2</sub>] (Lin *et al.*, 1997).

The angles O2—C8—C9 [116.8(4)°] and C8—C9—N1 [115.7(4)°] are reduced substantially below the normal value of 120° found at *sp*<sup>2</sup>-hybridized C or N. The angle around W [N1—W—O2 73.8(1)°] at the vertex of the nearly planar five-membered ring is smaller than expected for ideal octahedral geometry. This deviation is probably due to the substitution of a W—O bond by a much longer W—N coordination bond thereby allowing a smaller angle at W. This angle is larger than that in W(QBr)<sub>4</sub> [71.7(2)°; QBr is 5-bromo-8-quinolinolate; Bonds *et al.*, 1971] because there is more steric hindrance in W(QBr)<sub>4</sub>. A C—H...O hydrogen bond joins molecules of the title complex into a two-dimensional network parallel to (001).

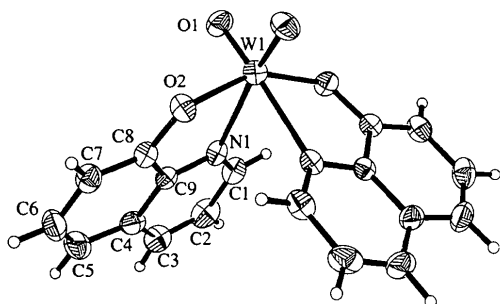


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

## Experimental

Hydrothermal treatment of carbonyl tungsten (0.2 mmol), 8-quinolinol (0.2 mmol) and methanol (5 ml) at 338 K for 1 d yielded two kinds of crystal. One is the title compound which is a golden yellow prismatic crystalline product; the yield was 14.5% based on carbonyl tungsten. The other is a bright-purple block crystalline product which will be discussed elsewhere.

### Crystal data

[WO<sub>2</sub>(C<sub>9</sub>H<sub>6</sub>NO)<sub>2</sub>]

*M<sub>r</sub>* = 504.15

Monoclinic

*C*2/*c*

*a* = 13.3506(3) Å

*b* = 9.4397(1) Å

*c* = 13.5106(3) Å

$\beta$  = 109.566(1)°

*V* = 1604.36(5) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 2.087 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 4538 reflections

$\theta$  = 2.70–28.31°

$\mu$  = 7.23 mm<sup>-1</sup>

*T* = 293(2) K

Slab

0.20 × 0.18 × 0.08 mm

Golden yellow

### Data collection

Siemens SMART CCD area-detector diffractometer

$\omega$  scans

Absorption correction:

empirical (SADABS);

Sheldrick, 1996)

*T<sub>min</sub>* = 0.307, *T<sub>max</sub>* = 0.561

5573 measured reflections

1993 independent reflections

1804 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.047

$\theta_{max}$  = 28.3°

*h* = -16 → 17

*k* = -12 → 12

*l* = -17 → 11

### Refinement

Refinement on *F*<sup>2</sup>

*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.035

*wR*(*F*<sup>2</sup>) = 0.089

*S* = 1.04

1993 reflections

114 parameters

H atoms constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0518*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 1.52 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -1.88 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for*

*Crystallography* (Vol. C)

Table 1. Selected geometric parameters and hydrogen-bonding geometry (Å, °)

W1—O1	1.722(4)	O2—C8	1.355(6)	
W1—O2	1.968(4)	N1—C1	1.328(6)	
W1—N1	2.336(4)	N1—C9	1.341(6)	
O1'—W1—O2	93.6(2)	O1—W1—N1	89.1(2)	
O1—W1—O2	103.5(2)	O2—W1—N1	73.8(1)	
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2A...O2 <sup>ii</sup>	0.93	2.49	3.344(8)	153

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ .

The highest peak in the difference Fourier map is at a distance of 0.98 Å from W.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and PLATON (Spek, 1990).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship. This work was supported by a grant for a key research project from the State Science and Technology Commission and the National Nature Science Foundation of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1319). Services for accessing these data are described at the back of the journal.

## References

- Ali, S. I. & Yunhir, N. K. S. (1993). *Thermochim. Acta*, **224**, 247–259.  
 Barton, R. J., Dabeka, R. W., Shengzhi, H., Mihichuk, L. M., Pizzey, M., Robertson, B. E. & Wallace, W. J. (1983). *Acta Cryst.* **C39**, 714–717.

- Bellavance, P. L., Corey, E. R., Corey, J. Y. & Hey, G. W. (1977). *Inorg. Chem.* **16**, 462–467.
- Bonds, W. D., Acher, R. D. & Hamilton, W. C. (1971). *Inorg. Chem.* **10**, 1764–1773.
- Klebe, G. & Tran Qui, D. (1984). *Acta Cryst.* **C40**, 476–479.
- Lin, Z. G., Huang, X. Y., Chi, L. S., Chen, H. Y. & Zhuang, H. H. (1997). *Chin. J. Struct. Chem.* **16**, 78–80.
- Marcel, B. & Rene, P. (1950). *Anal. Chim. Acta*, **4**, 267–285.
- Sawitzki, G., von Schnering, H. G., Kummer, D. & Seshadri, T. (1978). *Chem. Ber.* **111**, 3705–3710.
- Schneider, H. O. & Roselli, M. E. (1970). *An. Asoc. Quim. Argent.* **58**, 191–205.
- Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

*Acta Cryst.* (1999). **C55**, 2039–2041

### L-Argininium tris(acetato-*O,O'*)dioxouranium(III)–acetic acid–water (1/1/1)

M. RAMOS SILVA,<sup>a</sup> A. MATOS BEJA,<sup>a</sup> J. A. PAIXÃO,<sup>a</sup>  
L. ALTE DA VEIGA<sup>a</sup> AND J. MARTIN-GIL<sup>b</sup>

<sup>a</sup>*Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3000 Coimbra, Portugal, and* <sup>b</sup>*ETSII, Departamento de Química Inorgánica, Paseo del Cauce, s/n, SP-4701 Valladolid, Spain. E-mail: jap@pollux.fis.uc.pt*

(Received 2 September 1999; accepted 15 September 1999)

#### Abstract

The uranyl ion in the title compound, (C<sub>6</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub>)[UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>3</sub>]·C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>·H<sub>2</sub>O, is sixfold coordinated by three bidentate acetic acid ions. The O atoms form a hexagonal bipyramidal arrangement around the U atom. The non-crystallographic symmetry of the cation is approximately *D*<sub>6h</sub>. The cation is a positively charged zwitterion. The side chain of the amino acid has a conformation where the C<sub>γ</sub> atom is in a staggered *trans* position relative to the carboxyl group. An intricate three-dimensional network of hydrogen bonds interlinks the ions and the solvent molecules.

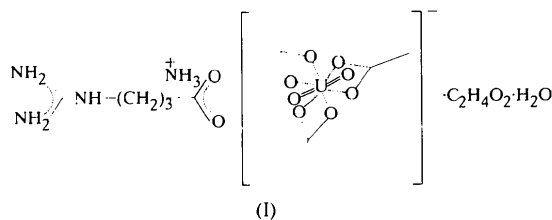
#### Comment

The uranyl oxocation UO<sub>2</sub><sup>2+</sup> has a rich solution chemistry, easily forming oligomers and different types of complexes with a great variety of counter-ions (Denning, 1983). There has been much work related to the study of different chelating agents of uranyl and

mineral-surface sorption complexes, driven by the problem of radioactive waste treatment.

Uranyl acetate is commonly used in the preparation of samples to be studied by electron microscopy. Animal tissues, fibres or DNA filaments are stained with uranyl acetate, a process which is one of the most effective and least damaging for staining samples (Schmitz *et al.*, 1994).

Uranyl binds to selective amino acids in proteins, a property which has been used for multiple anomalous dispersion (MAD) phasing in protein crystallography. Uranyl often binds to the protein at the same sites as other cations, *e.g.* Ca<sup>2+</sup>, in living cells (Shapiro *et al.*, 1995), which justifies the renewed interest in the study of the interaction between uranyl and amino acids. We report here the structure of the title compound, (I), L-Arg<sup>+</sup>(Ac<sub>3</sub>UO<sub>2</sub>)<sup>-</sup>·H<sub>2</sub>O·AcH, which crystallizes in the space group *P*2<sub>1</sub> with two formula units per cell.



The uranyl cation in (I) is sixfold coordinated by three bidentate acetic acid anions. The O atoms form a hexagonal bipyramidal arrangement around the U atom. The carboxy atoms lie approximately on a plane containing the U atom, with the exception of O8, which is slightly tilted out of the plane with a deviation of 0.165 (9) Å from the least-squares plane. The overall symmetry of the tris(acetato)dioxouranium anion is close to, but not exactly, *D*<sub>3h</sub>. The tris(acetato)dioxouranium ion often occurs with the U atom sitting on a threefold axis, imposing a coplanar arrangement of the carboxyl O atoms and a linear configuration of the core uranyl ion. This is the case in sodium and potassium tris(acetato)dioxouranate (Navaza *et al.*, 1991; Anisimova *et al.*, 1997). The uranyl ion is linear, the O1—U—O2 bonding angle being 179.6 (3)°. The U—O2 [1.755 (6) Å] distance is larger than the U—O1 distance [1.744 (6) Å], which may be due to the fact that O2 is involved in a hydrogen bond with a water molecule. Other U—O distances vary between 2.441 (4) and 2.490 (4) Å. While the uranyl O atoms vibrate in an isotropic way, the acetate atoms exhibit the largest atomic displacement parameter almost perpendicular to the equatorial plane of the uranyl ion.

The cations exist as positively charged zwitterions, in which the guanidyl and amino groups are protonated and the carboxyl groups deprotonated. The side chain of arginine can assume many different conformations on account of its length and flexibility. The torsion angles which define the conformation observed in this structure