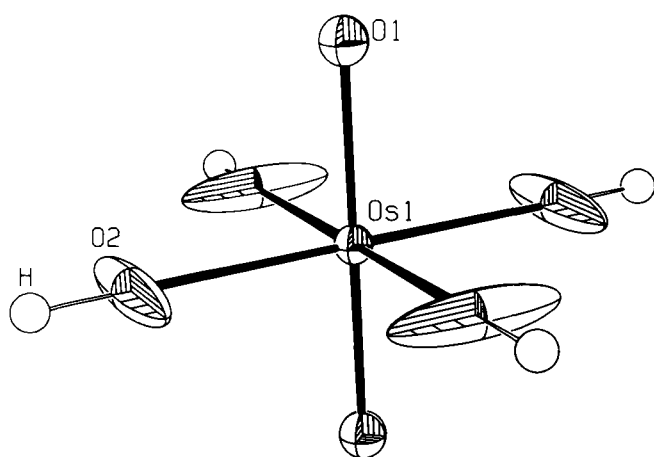


Redetermination of the crystal structure of potassium *trans*-(dioxo)-tetra(hydroxo)osmate(VI), $K_2[Os(OH)_4(O)_2]$

R. K. Murmann* and C. L. Barnes

University of Missouri, Department of Chemistry, E. O. Schlemper X-ray Laboratory, Columbia, MO 65211, USA

Received March 23, 2002, accepted and available on-line May 21, 2002; CSD-No. 409612



Abstract

$H_4K_2O_6Os$, tetragonal, $I4/mmm$ (No. 139), $a = 5.5856(4)$ Å, $c = 9.417(1)$ Å, $V = 293.8$ Å³, $Z = 2$, $R_{gt}(F) = 0.032$, $wR_{ref}(F^2) = 0.082$, $T = 173$ K.

Source of material

The crystalline product was prepared by the reaction of a slight excess of KNO_2 on a solution of OsO_4 dissolved in 2 molar KOH. After about 6 days of standing at room temperature crystals began to form. After another seven days the crystals were collected and dried in a stream of dry nitrogen. Yield about 80% of theory. This procedure was originally described in [1]. The crystalline material was stable in dry air for extended periods. It shows strong IR absorption bands at 3300, 1070 and 803 cm^{-1} .

Discussion

This compound is interesting theoretically as one of a few high oxidation state *trans*-dioxo complexes but also because it is the starting material toward many Os(VI) organic ligand complexes [2–4].

The structure was first studied in 1962 [5] but the space group was questionable and the estimated errors found were larger than presently attainable. The space group ($I4/mmm$) was strongly suggested by the data averaging. Using less symmetrical space groups including $I4/m$, as the previous study suggested [5], did

not improve the agreement factor nor the anisotropy of O2. The residual electron densities are slightly higher than usual due most likely to imperfections in the absorption correction. There was no evidence of twinning or abnormally shaped reflections. The hydrogen atom was located from an electron-density map and its coordinates and isotropic temperature factor were stable in the least-squares calculations. Its inclusion significantly lowered the agreement factor. However we are not confident of the Os–O–H angle ($180(2)^\circ$) because of the slightly elliptical nature of O2. O2 is elongated in the equatorial plane by a factor of 1.7 compared to the other two directions suggesting some slight disorder. The electron density map of the region occupied by O2 showed a single peak. The estimated separation between two half-occupied anisotropic oxygens is 0.45 Å, too small to be refined by least-squares analysis. We attribute the elongation of O2 to a small rotation around the O1–Os–O1 axis which may be static or dynamic. The yl-oxygens are appreciably closer to the metal (1.75(2) Å) than are the OH-oxygens (1.99(2) Å) compared to 1.77 Å, 2.03 Å, respectively, in [5]. The structure is dominated by strong ionic K–O bonding and there is no appreciable intra or intermolecular hydrogen bonding.

Table 1. Data collection and handling.

| | |
|---|--|
| Crystal: | dark purple octahedron, size $0.10 \times 0.13 \times 0.13$ mm |
| Wavelength: | Mo K_α radiation (0.71073 Å) |
| μ : | 230.75 cm^{-1} |
| Diffractometer, scan mode: | Siemens SMARTCCD, ω |
| $2\theta_{max}$: | 54.16° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 1012, 116 |
| Criterion for I_{obs} , $N(hkl)_{gt}$: | $I_{obs} > 2 \sigma(I_{obs})$, 116 |
| $N(param)_{refined}$: | 15 |
| Programs: | SHELXS-97 [6], SHELXL-97 [7], SADABS [8] |

Table 2. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | x | y | z | U_{iso} |
|------|------|---------|---|---|-----------|
| H | 8h | 0.86(3) | x | 0 | 0.03(6) |

* Correspondence author (e-mail: murmannr@missouri.edu)

Table 3. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | x | y | z | U ₁₁ | U ₂₂ | U ₃₃ | U ₁₂ | U ₁₃ | U ₂₃ |
|-------|------|----------|-----|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Os(1) | 2b | 1/2 | 1/2 | 0 | 0.0106(8) | U ₁₁ | 0.0121(9) | 0 | 0 | 0 |
| K(1) | 4d | 0 | 1/2 | 3/4 | 0.017(2) | U ₁₁ | 0.015(2) | 0 | 0 | 0 |
| O(1) | 4e | 1/2 | 1/2 | -0.185(2) | 0.017(5) | U ₁₁ | 0.018(8) | 0 | 0 | 0 |
| O(2) | 8h | 0.752(3) | x | 0 | 0.12(2) | U ₁₁ | 0.016(5) | -0.11(2) | 0 | 0 |

Acknowledgment. We wish to express our appreciation to The Department of Chemistry, University of Missouri for financial support.

References

1. Frey, E.: Über das Osmium. *J. Prakt. Chem.* **33** (1844) 406-416.
2. Gibbs, L.: On Osmyl-Ditetramin. *Amer. Chem. J.* **3** (1881) 233-238.
3. Malin, J.; Taube, H.: The ion dihydridobis(ethylenediamine)osmium(IV). *Inorg. Chem.* **10** (1971) 2403-2406.
4. Malin, J. M.; Schlemper, E. O.; Murmann, R. K.: Studies of the Ion *trans*-Dioxobis(ethylenediamine)Osmium(VI). X-ray Diffraction and Aqueous Oxygen-18. Exchange. *Inorg. Chem.* **16** (1977) 615-619.
5. Avtomyan, L. O.; Andrianov, V. G.; Porai-Kohits, M. A.: The structure of potassium hydroxoosmate K₂[Os(O)₂(OH)₄]. *Zh. Strukt. Khim.* **3** (1962) 685-690.
6. Sheldrick, G. M.: SHELXS-97. Program for the solution of crystal structures. University of Göttingen, Germany 1997.
7. Sheldrick, G. M.: SHELXL-97. Program for refining crystal structures. University of Göttingen, Germany 1997.
8. SADABS, based on Blessing, R. H.: *Acta Crystallogr. A* **51** (1995) 33-39.