CHEMISTRY LETTERS, pp. 2327-2330, 1987.

Preparation of Tungsten(V) Aqua Ion, $W_2O_2S_2(aq)^{2+}$, and X-Ray Structure of Di-μ-sulfido-bis[(cysteinato)oxotungstate(V)] Ion, $[W_2O_2S_2(cys)_2]^{2-}$

Takashi SHIBAHARA,* Yukiharu IZUMORI, Reiko KUBOTA,
and Hisao KUROYA
Department of Chemistry, Okayama University of Science,
1-1 Ridai-cho, Okayama 700

Di-μ-sulfido tungsten(V) dimers, $[W_2O_2S_2(cys)_2]^{2-}$ (**1**) and $W_2O_2S_2(aq)^{2+}$ (**2**) have been prepared and characterized. The structure of the former has been determined by the X-ray crystal structure analysis. The W-W bond distance is 2.843(1) Å. Peak positions of electronic spectra are : 428 nm (ε = 259 M^{-1} cm^{-1} per dimer; 1 M = 1 mol dm^{-3}), 330_{sh} (3920), and 276 (10760) for **1**; 435 (144), 320 (2640), and 263 (7180) for **2**.

Molybdenum(V) aqua dimers, $Mo_2O_4(aq)^{2+}$,1) $Mo_2O_3S(aq)^{2+}$,2) and $Mo_2O_2S_2(aq)^{2+}$,3) have been studied extensively. These aqua ions† can be prepared by the aquation of the corresponding cysteinato complexes, which have been widely used as model compounds of molybdo-enzymes4) or as starting materials of other molybdenum-containing complexes.5) The complexes having Mo_2S_4 core have also been reported.6) However, studies on tungsten(V) dimer are relatively rare: $[W_2O_2S_2Cl_4]^{2-}$ 7) is the only compound having $W_2O_2S_2$ core and a few compounds with W_2O_4 or W_2S_4 have been known.8) Very recently, preparation and properties of di-μ-oxotungsten(V) aqua dimer, $W_2O_4(aq)^{2+}$, are described9) and the existence of an enzyme containing tungsten and inorganic sulfur is also known.10)

We now report the preparation and characterization of a di-μ-sulfido cysteinatooxotungsten(V) dimer, $[W_2O_2S_2(cys)_2]^{2-}$(**1**), and the corresponding aqua ion, $W_2O_2S_2(aq)^{2+}$ (**2**). The presence of the core structure has been confirmed by the X-ray crystal structure determination of the former. Nothing has been known of the formation of **1** and **2** and these complexes will be of good use in the preparation of $W_2O_2S_2$-core complexes.11)

Potassium salt of **1** was prepared as follows. No air-free condition is required for the preparation of **1** and **2**. Concentrated HCl (8 mL) was added to an aqueous solution (50 mL) containing $(NH_4)_2WS_4$ (5 g).12) L-cysteine hydrochloride monohydrate (6 g) was added to the solution, whose pH was then adjusted to ca. 7 by use of ca. 10 M KOH. The color of the solution turned from brown to green. The resultant solution was heated for ca. 20 min, cooled to room temperature, and

---

† The term "aqua ion" is used here for species in which bridging sulfur and oxygen atom(s) exist and other ligands are only water.

filtered. Then, KCl (5 g) was added to the filtrate, which was kept in a refrigerator overnight. Brown crystals deposited were filtered off and washed successively with methanol and diethyl ether. Recrystallization from hot water gave orange crystals. Yield was ca. 2.2 g (35%) after recrystallization. Anal. Calcd for $K_2[W_2O_2S_2(SCH_2CH(NH_2)CO_2)_2]\cdot 5H_2O$: K, 8.98; N, 3.21; C, 8.27; H, 2.31%. Found: K, 8.98; N, 3.36; C, 8.36; H, 2.31%.

X-Ray crystal structure analysis[13)] revealed the existence of a di-μ-sulfido dinuclear tungsten core structure in $[W_2O_2S_2(cys)_2]^{2-}$ ion (Fig. 1). The structure of this anion has an approximate symmetry of C_2 as seen in the structures of $[Mo_2O_4(cys)_2]^{2-}$,[14)] $[Mo_2O_3S(cys)_2]^{2-}$,[15)] and $[Mo_2O_2S_2(cys)_2]^{2-}$.[16)] The W-W distance (2.843(1) Å) is distinctly longer than that in $[W_2O_4(edta)_2]^{2-}$ (2.55 Å), but close to that in $[W_2O_2S_2Cl_4]^{2-}$ (2.844(1) Å).

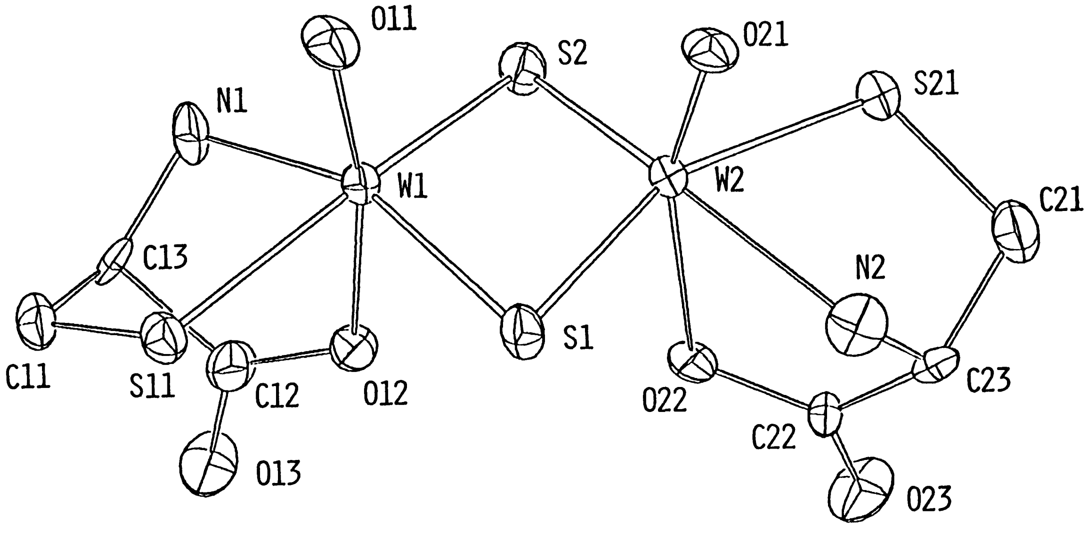

Fig. 1. Perspective view of $[W_2O_2S_2(cys)_2]^{2-}$. Selected bond distances/Å: W1-W2, 2.843(1); W1-S1, 2.381(5); W1-S2, 2.378(5); W1-S11, 2.477(5); W1-O11, 1.76(2); W1-O12, 2.22(2); W1-N1, 2.16(2); W2-S1, 2.327(5); W2-S2, 2.265(5); W2-S21, 2.549(5); W2-O21, 1.73(2); W2-O22, 2.27(2); W2-N2, 2.33(2)

Two methods were effectively employed for the preparation of **2**. Method A: One tenth gram of the cysteinato complex was dissolved in 1 M $HClO_4$ (40 mL) and Sephadex G-15 column chromatography (1 M $HClO_4$) was applied, the yellow band being collected. Method B: $(NH_4)_2WS_4$ (1 g) was dissolved in 1 M $HClO_4$ (40 mL). Sephadex G-15 column chromatography was applied as in Method A. Electronic spectra of **1** and **2** are shown in Fig. 2 together with those of the corresponding molybdenum(V) dimers. Peak positions, $\lambda_{max,nm}$ (ε / M^{-1} cm^{-1} per dimer), are : 428 (259), 330_{sh} (3920), and 276 (10760) for **1**; 435 (144), 320 (2640), and 263 (7180) for **2**. The peak positions of **1** and **2** are shifted as a whole towards shorter wavelengths as compared to the corresponding molybdenum dimers, and additionally, the spectra of the tungsten dimers have characteristic peaks at about 430 nm, while the molybdenum dimers have no peaks in the visible region. Little red-shift in the visible region is observed in the peak position of **2** compared to that of $W_2O_4(aq)^{2+}$, while a large red-shift is observed on the substitution of sulfur(s) for bridging oxygens in the complexes having $Mo_2O_{4-n}S_n$ core.[17)] The cysteinato complex **1** is fairly resistant toward air oxidation, not only in the solid state but also in the solution. The aqua ion **2** in 1 M $HClO_4$ is stable in low concentration under air. The absorbance of the aqua ion (2 x 10^{-3} M) remains unchanged for 2 days under air. However, its absorbance increases gradually, when the concentration of the aqua ion exceeds ca. 3 x 10^{-3} M. The reason why the absorbance of the solution at higher concentration increases is not clear at present. The aqua ion in 1 M HCl or in 1 M HPTS (p-toluenesulfonic acid) also has absorption peaks at ca. 435 nm. The solution of the aqua ion in HPTS becomes turbid gradually under both air and dinitrogen atmosphere.

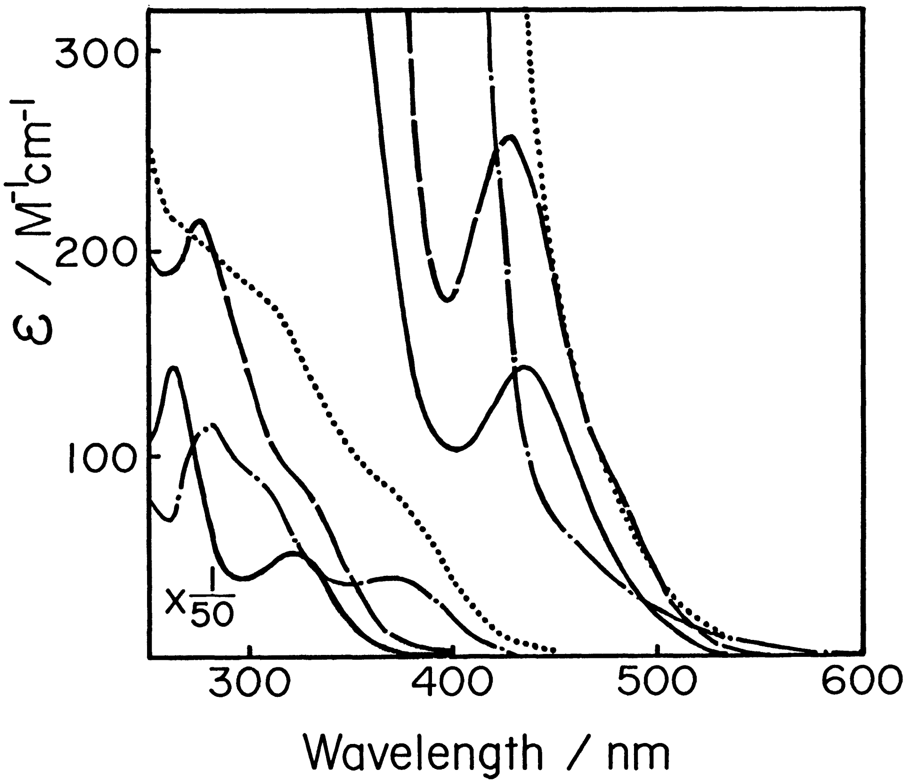

Fig. 2. Electronic spectra.

——————— $W_2O_2S_2(aq)^{2+}$ in 1 M $HClO_4$

—— —— —— $[W_2O_2S_2(cys)_2]^{2-}$ in water

—— - —— - — $Mo_2O_2S_2(aq)^{2+}$ in 1 M $HClO_4$

-------------- $[Mo_2O_2S_2(cys)_2]^{2-}$ in water

This work was supported by a Grant-in-Aid for Scientific Research (No. 62470043) from the Ministry of Education, Science and Culture.

References

1) M. Ardon and A. Pernick, Inorg. Chem., 12, 2484 (1973); Y. Sasaki and A. G.

Sykes, J. Chem. Soc., Dalton Trans., 1974, 1468.

2) V. R. Ott, D. S. Swieter, and F. A. Schultz, Inorg. Chem., 16, 2538 (1977); K. Z. Suzuki, Y. Sasaki, S. Ooi, and K. Saito, Bull. Chem. Soc. Jpn., 53, 1288 (1980); T. Shibahara, S. Ooi, and H. Kuroya, ibid., 55, 3742 (1982).

3) B. Spivack and Z. Dori, J. Chem. Soc., Chem. Commun., 1973, 909; Ref. 2a; F. A. Armstrong, T. Shibahara, and A. G. Sykes, Inorg. Chem., 17, 189 (1978).

4) E. I. Stiefel, Prog. Inorg. Chem., 22, 1 (1977).

5) For example, T. Shibahara and H. Kuroya, Polyhedron, 5, 357 (1986).

6) For example, J. Bernholc and E. I. Stiefel, Inorg. Chem., 25, 3876 (1986).

7) M. G. B. Drew, E. M. Page, and D. A. Rice, Inorg. Chim. Acta, 76, L33 (1983).

8) For example, $[W_2O_4(edta)]^{2-}$: J. Novak and J. Podlaha, J. Inorg. Nucl. Chem., 36, 1061 (1974); S. Khalil, B. Sheldrick, A. B. Soares, and A. G. Sykes, Inorg. Chim. Acta, 25, L83 (1977); S. Khalil and B. Sheldrick, Acta Crystallogr., Sect. B, 34, 3751 (1978). $[W_2S_4(S_2C_2H_4)_2]^{2-}$: W.-H. Pan, T. Chandler, J. H. Enemark, and E. I. Stiefel, Inorg. Chem., 23, 4265 (1984). $[W_2S_4(S_4)_2]^{2-}$: S. A. Cohen and E. I. Stiefel, Inorg. Chem., 24, 4657 (1985). $[W_2S_4(WS_4)_2]^{2-}$: F. Secheresse, J. Lefebvre, J. C. Daran, and Y. Jeannin, Inorg. Chem., 21, 1311 (1982).

9) Private communication from Prof. Sykes: C. Sharp, E. F. Hills, and A. G. Sykes, J. Chem. Soc., Dalton Trans, in press; C. Sharp and A. G. Sykes, to be published.

10) I. Yamamoto, T. Saiki, S.-M. Liu, and L. G. Ljungdahl, J. Biol. Chem., 258, 1826 (1983).

11) For example, ethylenediaminetetraacetato (edta) complex, $[W_2O_2S_2(edta)]^{2-}$, can be prepared from **1** and $Na_2H_2edta \cdot 2H_2O$.

12) J. M. McDonald, G. D. Frisen, L. D. Rosenheim, and W. E. Newton, Inorg. Chim. Acta, 72, 205 (1983).

13) Crystal data: monoclinic system, space group $P2_1$, $a = 9.670(1)$ Å, $b = 15.993(2)$ Å, $c = 6.893(1)$ Å, $\beta = 95.02(1)°$, $V = 1062.0(3)$ Å^3, $Z = 2$. Intensity data were collected on a RIGAKU automated four-circle diffractometer by use of graphite-monochromated Mo-Kα radiation on the $2\theta \leq 65°$ range. The coordinates of W's and S's were determined by means of MULTAN, and the remaining nonhydrogen atoms were located from difference maps. The current R value is 0.0649 for 3696 reflections($F_o \geq 6\sigma(F_o)$). A list of atomic coordinates, thermal parameters, bond distances and angles can be obtained from the author (T. S.) on request.

14) J. R. Knox and C. K. Prout, Acta Crystallogr., Sect. B, 25, 1857 (1969).

15) T. Shibahara, H. Kuroya, K. Matsumoto, and S. Ooi, Bull. Chem. Soc. Jpn., 60, 2277 (1987); Mo-Mo = 2.718(1) Å.

16) D. H. Brown and J. A. D. Jeffreys, J. Chem. Soc., Dalton Trans., 1973, 732.

17) For example, Refs. 2-4.

(Received September 8, 1987)