Inorganica Chimica Acta, *127* (1987) L39–L40 L39

Preparation of Incomplete Cubane-type Sulfur-capped Tungsten(IV) Aqua Ion, $W_3OS_3^{4+}$, and X-ray Structure of $K_2[W_3OS_3\{N(CH_2CO_2)_2(CH_2CO_2H)\}_3]\cdot KCl\cdot 7H_2O$

TAKASHI SHIBAHARA*, ATSUSHI TAKEUCHI
and HISAO KUROYA

Department of Chemistry, Okayama University of Science,
1-1 Ridai-cho, Okayama 700, Japan

(Received October 2, 1986)

We have recently reported on the preparation and properties of the triangular tungsten(IV) aqua ion, $W_3S_4^{4+}$ [1]. Only a few papers have been published on triangular tungsten complexes with sulfur bridge(s): $W_3S_4^{4+}$ aqua ion [1], $[W_3S_4(NCS)_9]^{5-}$ [1], and $[W_3(\mu_2\text{-}O)_3(\mu_3\text{-}S)(NCS)_9]^{5-}$ [2] are all reported so far, while a sequence of incomplete cubane-type molybdenum complexes with sulfur bridge(s), $Mo_3O_{4-n}S_n^{4+}$ (n = 1–4), are known [3–12].

We describe here the preparation and characterization of an incomplete cubane-type sulfur-capped tungsten(IV) aqua ion, $W_3(\mu_2\text{-}O)(\mu_2\text{-}S)_2(\mu_3\text{-}S)^{4+}$, and the X-ray structure analysis of a derivative complex $K_2[W_3OS_3(Hnta)_3]\cdot KCl\cdot 7H_2O$ (**1**), where H_3nta stands for nitrilotriacetic acid.

Two methods are effective for the preparation of the $W_3OS_3^{4+}$ aqua ion. Method A: the procedure is the same as that in the preparation of the $W_3S_4^{4+}$ aqua ion up to the step of the Sephadex column chromatography [1]. The first red–purple band (λ_{max} = 540 nm *in* 1 M HCl) was purified by use of a Dowex 50W-X4 cation exchanger (2 M HCl). An HPTS (*p*-toluenesulfonic acid) solution of the ion was obtained as described elsewhere [13]. This aqua ion is stable toward air oxidation. Method B: $(NH_4)_2WS_4$ (1 g) dissolved in a small amount of water was added to 3 M HCl (200 ml) containing $K_3[W_2Cl_9]$ (2.3 g) [14]. The solution was heated with stirring over 90 °C for 2 h, and then air was passed through the solution for one day at room temperature. After filtration, Sephadex G-15 column chromatography (1 M HCl) was applied and the resultant red–purple solution was purified as in Method A.

Preparation of **1** is as follows. One half gram (2.6 mmol) of nitrilotriacetic acid dissolved in a minimum amount of 10 M KOH solution was added drop by drop into 2 M HCl solution of the aqua complex (50 ml, *ca.* 2.3 mM with the complex) and the pH of the resultant solution was raised to 1.2 by the addition of 10 M KOH. After being kept at room temperature for one day, the solution was filtered, diluted with water, and absorbed on a Dowex 1-X2 anion exchanger. Elution by 2 M KCl gave a purple solution, the pH of which was succeedingly adjusted to 1.2 by the addition of 2 M HCl. Purple crystals were deposited by placing the solution in a refrigerator. *Anal.* Found (calc.): N, 2.75 (2.78); C, 14.21 (14.31); H, 2.16 (2.33); K, 7.82 (7.76)%.

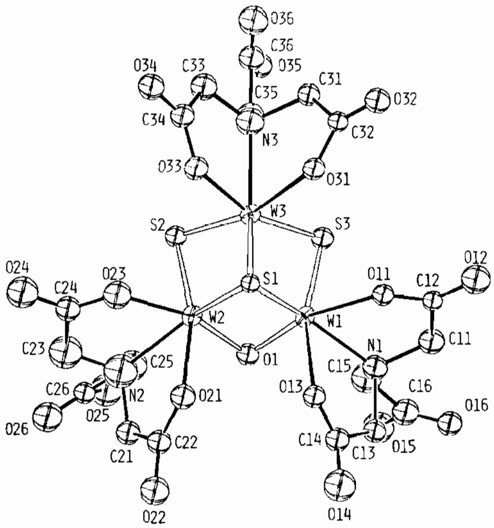

Fig. 1. Perspective view of $[W_3OS_3(Hnta)_3]^{2-}$ with selected bond distances (Å): W1–W2, 2.620(1); W1–W3, 2.719(1); W2–W3, 2.728(1); W1–S1, 2.336(6); W2–S1, 2.353(6); W3–S1, 2.343(6); W1–S3, 2.313(6); W1–O1, 1.947(14); W2–S2, 2.308(6); W2–O1, 1.956(14); W3–S2, 2.318(6); W3–S3, 2.319(6); W–N, 2.27(av.); W–O(ligand), 2.09(av.).

X-ray structure analysis* of **1** revealed the existence of an incomplete cubane-type $W_3(\mu_2\text{-}O)(\mu_2\text{-}S)_2(\mu_3\text{-}S)^{4+}$ core in it (Fig. 1) and supports the presence of the $W_3OS_3^{4+}$ aqua ion (probably $[W_3OS_3(H_2O)_9]^{4+}$) in solution. The complex anion, $[W_3OS_3(Hnta)_3]^{2-}$, has an approximate mirror plane. The W1–W2 distance is distinctly shorter than W1–W3 and W2–W3 distances, analogous to the case of $[Mo_3OS_3(ida)_3]^{2-}$ (H_2ida = iminodiacetic acid) [6b]. The W1–W2 distance is close to the W–W distance in $[W_3O_3S(NCS)_9]^{5-}$ [2] and

---

*Author to whom correspondence should be addressed.

*The compound **1** crystallizes in triclinic system, space group $P\bar{1}$ with cell dimensions a = 14.876(3), b = 15.199(3), c = 11.068(2) Å, α = 109.86(2), β = 97.23(2), γ = 112.70(2)°, V = 2074.0(9) Å^3, Z = 2, D_c = 2.446 g cm^{-3}. Intensity data were collected on an automated four-circle diffractometer by use of graphite-monochromated Mo Kα radiation. The coordinates of W were determined by means of MULTAN and the remaining non-hydrogen atoms were located from difference maps. The current R value is 0.0610 for 4114 reflections ($F_o \geqslant 8\sigma(F_o)$).

0020-1693/87/$3.50

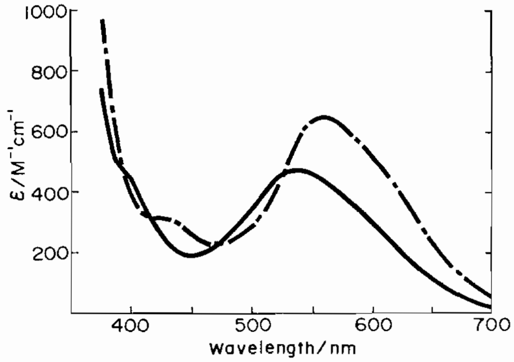

Fig. 2. Electronic spectra: —— $W_3OS_3^{4+}$ in 2 M HPTS; – · – $[W_3OS_3(Hnta)_3]^{2-}$ in water.

the W1–W3 and W2–W3 distances are shorter than W–W distances in $[W_3S_4(NCS)_9]^{5-}$ [1].

The electronic spectrum of the $W_3OS_3^{4+}$ aqua ion is shown in Fig. 2 together with that of the nitrilotriacetato complex. The peak position of the aqua ion ($\lambda_{max} = 535$ nm, $\epsilon = 408$ M^{-1} cm^{-1} per trimer) is blue-shifted, as compared to that of the $W_3S_4^{4+}$ aqua ion ($\lambda_{max} = 560$ nm) [1] as is the case with $Mo_3OS_3^{4+}$ ($\lambda_{max} = 588$ nm) [3] and $Mo_3S_4^{4+}$ ($\lambda_{max} = 602$ nm) [6].

Supplementary Material

Atomic coordinates and thermal parameters are available from the authors on request.

References

1 T. Shibahara, K. Kohda, A. Ohtsuji, K. Yasuda and H. Kuroya, *J. Am. Chem. Soc., 108*, 2757 (1986).
2 Z. Dori, F. A. Cotton, R. Llusar and W. Schwotzer, *Polyhedron, 5*, 907 (1986).
3 T. Shibahara, H. Miyake, K. Kobayashi and H. Kuroya, *Chem. Lett.*, 139 (1986).
4 T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan and A. G. Sykes, *Inorg. Chim. Acta, 113*, L19 (1986).
5 F. A. Cotton, Z. Dori, R. Llusar and W. Schwotzer, *J. Am. Chem. Soc., 107*, 6734 (1985).
6 (a) T. Shibahara and H. Kuroya, *Abstracts of Papers, 5th International Conference on the Chemistry and Uses of Molybdenum*, Newcastle-upon-Tyne, U.K., July 1985; (b) *Polyhedron, 5*, 357 (1986).
7 F. A. Cotton, R. Llusar, D. O. Marlar, W. Schwotzer and Z. Dori, *Inorg. Chim. Acta, 102*, L25 (1985).
8 (a) P. Kathirgamanathan, M. Martinez and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 953 (1985); (b) 1437 (1985).
9 A. Muller, R. Jostes, W. Eltzer, C.-S. Nie, E. Diemann, H. Bogge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S. J. Cyvin and B. N. Cyvin, *Inorg. Chem., 24*, 2872 (1985).
10 T. Shibahara, H. Hattori and H. Kuroya, *J. Am. Chem. Soc., 106*, 2710 (1984).
11 T. R. Halbert, K. McGauley, W.-H. Pan, R. S. Czernuszewicz and E. I. Stiefel, *J. Am. Chem. Soc., 106*, 1849 (1984).
12 N. C. Howlader, G. P. Haight, Jr., T. W. Hambley, G. A. Lawrance, K. M. Rahmoeller and M. R. Snow, *Aust. J. Chem., 36*, 377 (1983).
13 T. Shibahara, H. Akashi and H. Kuroya, *J. Am. Chem. Soc., 108*, 1342 (1986).
14 E. A. Heintz, in J. Kleinberg (ed.), 'Inorganic Syntheses', Vol. 7, McGraw-Hill, New York, 1963, p. 142.