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Incomplete Cubane-Type Sulfur-Capped Aqua Ion, $W_3O_2S_2{}^{4+}$ and X-Ray Structure of $Ba[W_3O_2S_2(N(CH_2CO_2)_2(CH_2CO_2H))_3]\cdot 9H_2O$

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A triangular tungsten(IV) aqua ion with sulfur bridges, $W_3O_2S_2{}^{4+}$, has been prepared and characterized. X-ray structure analysis of a derivative complex, $[W_3O_2S_2(Hnta)_3]^{2-}$ (H_3nta = nitrilotriacetic acid) has revealed that its core is of structure of $W_3(\mu_2\text{-}O)_2(\mu_2\text{-}S)(\mu_3\text{-}S)$. The electronic spectrum of the aqua ion has an absorption peak at 506 nm (ε = 381 M^{-1} cm^{-1} per trimer; 1 M = 1 mol dm^{-3}).

Few reports have appeared on incomplete cubane-type tungsten complexes with sulfur and/or oxygen bridges and the followings are all so far reported; $W_3S_4{}^{4+}$ aqua ion,¹⁾ $[W_3S_4(NCS)_9]^{5-}$,¹⁾ $W_3OS_3{}^{4+}$ aqua ion,²⁾ $[W_3(\mu_2\text{-}O)(\mu_2\text{-}S)_2(\mu_3\text{-}S)(Hnta)_3]^{2-}$,²⁾ $[W_3(\mu_2\text{-}O)_3(\mu_3\text{-}S)(NCS)_9]^{5-}$ ³⁾ and some oxo-bridged complexes with the W_3O_4 core.⁴⁾ On the other hand, a sequence of incomplete cubane-type molybdenum complexes with sulfur bridge(s), $Mo_3O_{4-n}S_n{}^{4+}$ (n = 1 - 4), has been obtained,⁵ ⁻ ¹⁵⁾ and many investigations on the $Mo_3O_4{}^{4+}$ aqua ion and its derivative complexes have been made.¹⁶⁾

We describe here the preparation and characterization of an incomplete cubane-type tungsten(IV) aqua ion, $W_3O_2S_2{}^{4+}$ (**1**) and the X-ray structure analysis of a derivative complex, $Ba[W_3(\mu_2\text{-}O)_2(\mu_2\text{-}S)(\mu_3\text{-}S)(Hnta)_3]\cdot 9H_2O$ (**2**).

$(NH_4)_2WS_4$¹⁷⁾ (1 g) dissolved in water (ca. 10 cm^3) was mixed with $K_3[W_2Cl_9]$¹⁸⁾ (3 g) in 3 M HCl (50 cm^3). The solution was heated with stirring over 90 °C for two hours.¹⁹⁾ After filtration, Sephadex G-15 column chromatography (1 M HCl) was applied and the resulting red solution of **1** was purified by use of a Dowex 50W-X8 cation exchanger (2 M HCl). Yield was ca. 18% based on total tungsten.²⁰⁾ An HPTS (p-toluenesulfonic acid) solution of the aqua ion also can be obtained as described elsewhere.⁵⁾ The aqua ion **1** is stable toward air oxidation.

Preparation of **2** is as follows. Nitrilotriacetic acid (0.3 g) dissolved in minimum amount of ca. 10 M KOH was added drop by drop to the aqua ion **1** (ca. 3 x 10^{-3} M, 100 cm^3) in 2 M HCl. After pH adjustment to 1.2 by the addition of KOH, the solution was kept at room temperature overnight and filtered. The filtrate was diluted and poured on a Dowex 1-X2 anion exchanger, and then the adsorbed product was eluted with 1 M $BaCl_2$ solution. The pH of the eluate was adjusted to 1.2 by the addition of 2 M HCl. Red purple crystals were deposited on standing the solution at room temperature for several days. Anal. Found (calcd): N, 2.75 (2.77); C, 14.27 (14.30); H, 2.33 (2.59)%.

The compound crystallizes in triclinic system, space group P$\bar{1}$ with cell dimensions a = 11.728(4) Å, b= 11.767(4) Å, c = 11.113(3) Å, α = 96.57(2)°, β = 98.64(3)°, γ = 99.64(2)°, V = 1982.2(11) Å^3, Z = 2. D_c = 2.538 g cm^{-3}. Intensity data (2θ ≤ 45°) were collected on a Rigaku AFC-6A four-circle diffractometer by use of graphite-monochromated Mo Kα radiation. The structure was solved by the direct method (MULTAN) and refined by least squares to a current R value of 0.0538 for 3509 reflections ($F_o \geq 6\sigma(F_o)$).[21] The existence of an incomplete cubane-type $W_3(\mu_2\text{-O})_2(\mu_2\text{-S})(\mu_3\text{-S})$ core in **2** is verified (Fig. 1). An approximate mirror plane is present in the complex anion. The W1-W2 (bridged by μ_2-S) distance is distinctly longer than the W1-W3 and W2-W3 (bridged by μ_2-O) distances as observed in other complexes with the incomplete cubane-type $M_3O_{4-n}S_n$ (M = Mo or W) core.[2,6,7] All the nitrogen atoms occupy the δ position compared to the case of $[Mo_3OS_3(HN(CH_2CO_2)_2)_3]^{2-}$.[6] One uncoordinated CO_2 group in each $Hnta^{2-}$ ligand

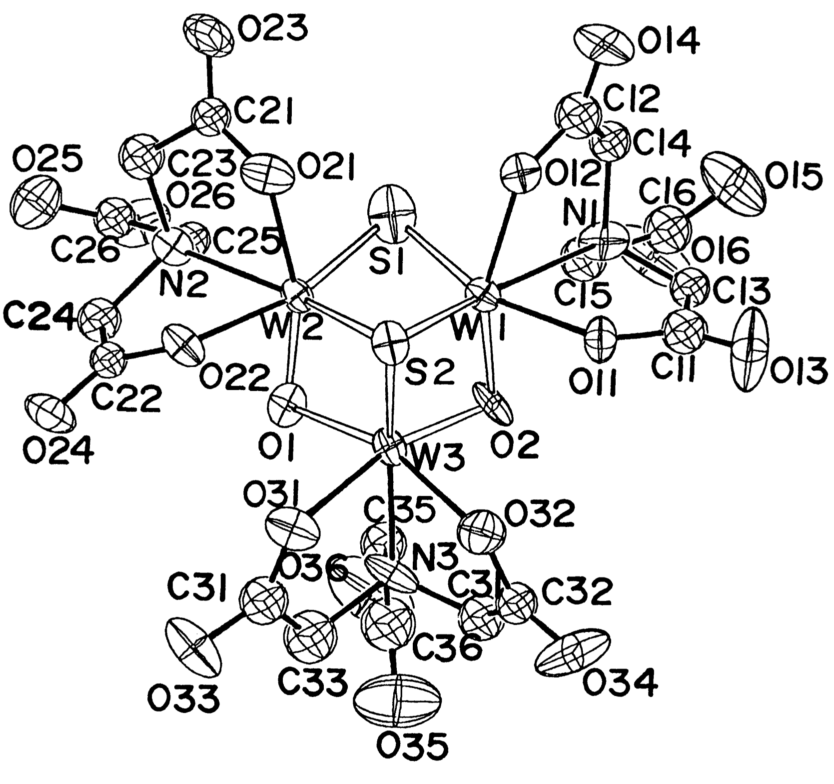

Fig. 1. Perspective view of $[W_3O_2S_2(Hnta)_3]^{2-}$. Selected bond distances/Å: W1-W2, 2.684(2); W1-W3, 2.612(2); W2-W3, 2.611(2); W1-S1, 2.264(8); W1-S2, 2.368(8); W2-S1, 2.286(9); W2-S2, 2.374(6); W3-S2, 2.383(6); W1-O2, 1.980(16); W2-O1, 2.036(18); W3-O1, 2.024(15); W3-O2, 1.978(16); W1-O11, 2.091(15); W1-O12, 2.129(16); W2-O21, 2.066(18); W2-O22, 2.097(17); W3-O31, 2.091(18); W3-O32, 2.081(16); W1-N1, 2.287(20); W2-N2, 2.273(17); W3-N3, 2.263(21).

has a longer (av. 1.33 Å) and a shorter (av. 1.20 Å) C-O bonds indicating the existence of three COOH groups in the whole complex anion.[22]

The electronic spectrum of the aqua ion **1** (λ_{max} = 506, ε = 381 M^{-1} cm^{-1} per trimer) is shown in Fig. 2 together with that of **2**. For comparison, the spectra of $W_3S_4{}^{4+}$ and $W_3OS_3{}^{4+}$ aqua ions are included. Red shift of absorption maxima and increse in ε values are observed when the number of sulfur atoms are increased in the incomplete cubane-type core.

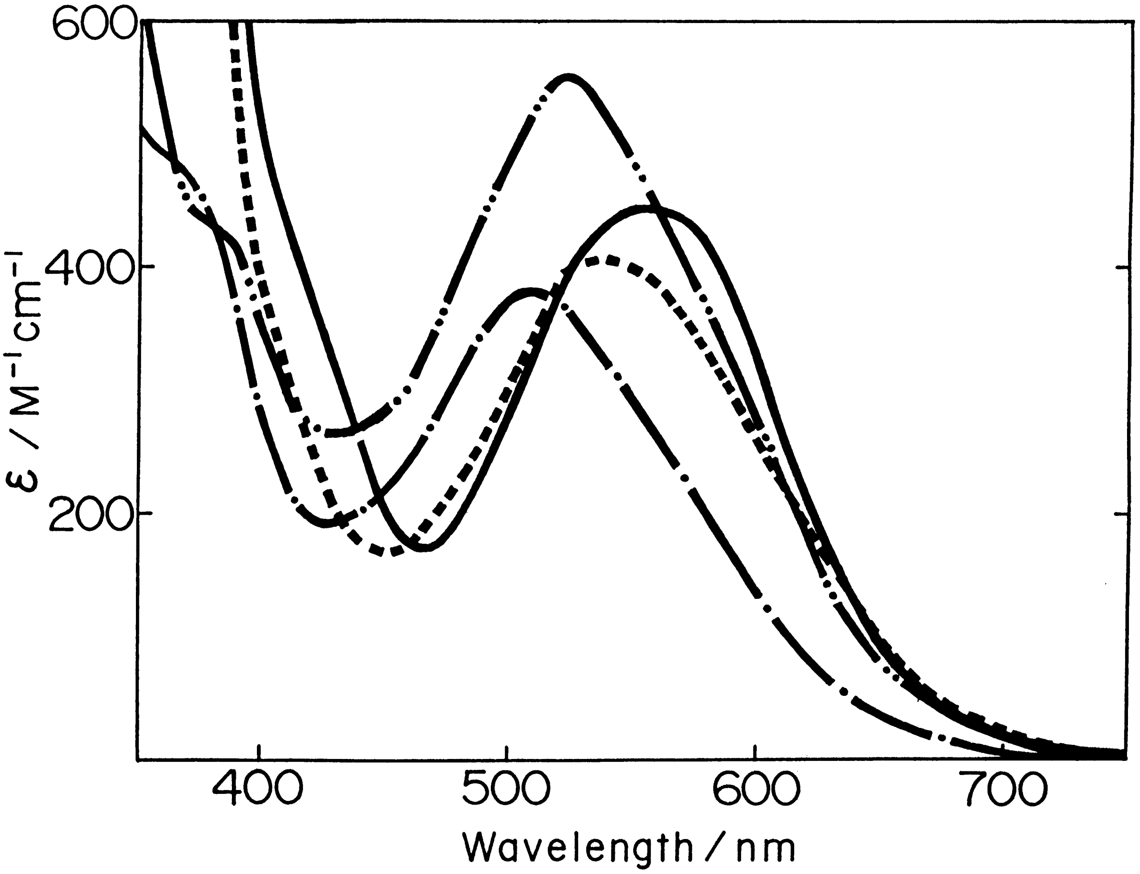

Fig. 2. Electronic spectra.

——— - ——— - ——— - $W_3O_2S_2{}^{4+}$(aq) in 2 M HPTS
——— - - ——— - - ——— $[W_3O_2S_2(Hnta)_3]^{2-}$ in water
— — — — — — — — — $W_3OS_3{}^{4+}$(aq) in 2 M HPTS
————————— $W_3S_4{}^{4+}$(aq) in 2 M HPTS

References

1) T. Shibahara, K. Kohda, A. Ohtsuji, K. Yasuda, and K. Kuroya, J. Am. Chem. Soc., 108, 2757 (1986).
2) T. Shibahara, A. Takeuchi, and H. Kuroya, Inorg. Chim. Acta, 127, L39 (1987).
3) Z. Dori, F. A. Cotton, R. Llusar, and W. Schwotzer, Polyhedron, 5, 907

(1986).

4) P. Chaudhuri, K. Wieghardt, W. Gebert, I. Jibril, and G. Huttner, Z. Anorg. Allg. Chem., 521, 23 (1985); M. Segawa and Y. Sasaki, J. Am. Chem. Soc., 107, 5565 (1985); R. Mattes and K. Mennemann, Z. Anorg. Allg. Chem., 437, 175 (1977).

5) T. Shibahara, H. Hattori, and H. Kuroya, J. Am. Chem. Soc., 106, 2710 (1984).

6) T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan, and A. G. Sykes, Inorg. Chim. Acta, 113, L19 (1986).

7) T. Shibahara, H. Miyake, K. Kobayashi, and H. Kuroya, Chem. Lett., 1986, 139.

8) T. Shibahara, H. Kuroya, "Abstract of Papers," 5th International Conference on the Chemistry and Uses of Molybdenum, Newcastle upon Tyne, England, July 1985, p. 59; T. Shibahara and H. Kuroya, Polyhedron, 5, 357 (1986).

9) F. A. Cotton, Z. Dori, R. Llusar, and W. Schwotzer, J. Am. Chem. Soc., 107, 6734 (1985).

10) P. Kathirgamanathan, M. Martinez, and A. G. Sykes, J. Chem. Soc., Chem. Commun., 1985, 953.

11) P. Kathirgamanathan, M. Martinez, and A. G. Sykes, J. Chem. Soc., Chem. Commun., 1985, 1437.

12) A. Muller, R. Jostes, W. Eltzner, C. Nie, E. Dieman, H. Bogge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogel, S. Che, and S. J. Cyvin, Inorg. Chem., 24, 2872 (1985).

13) H. Brunner, H. Kauermann, and J. Wacher, J. Organomet. Chem., 265, 189 (1984).

14) N. C. Howlader, G. P. Haight, Jr., T. W. Hambley, G. A. Lawrance, K. M. Rahomoller, M. R. Snow, Aust. J. Chem., 36, 377 (1983).

15) A. Muller and U. Reinsch, Angew. Chem., Int. Ed. Engl., 19, 72 (1980).

16) For example, S. F. Gheller, T. W. Hambley, R. T. C. Brownlee, M. J. O'Conner, M. R. Snow, A. G. Wedd, J. Am. Chem. Soc., 105, 1527 (1983); M. T. Paffet and F. C. Anson, Inorg. Chem., 22, 1347 (1983).

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

18) E. A. Heintz, "Inorganic Synthesis," ed by J. Kleinberg, McGraw-Hill, New York (1963), Vol. 7, p. 142.

19) Aeration is not required in this case: cf. Ref. 2.

20) Other products with incomplete cubane-type core are : $W_3O_3S^{4+}$ aqua ion (ca. 10%; unpublished result) and $W_3S_4{}^{4+}$ aqua ion (ca. 5%).

21) A list of atomic coordinates and thermal parameters can be obtained from the author (T. S.) on request.

22) The infrared spectrum has an absorption band at 1700 cm^{-1}.

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