Sulfur-capped Triangular Tungsten(IV) Aqua Ion, $W_3O_3S^{4+}$ and X-ray Structure of $K_2[W_3O_3S(N(CH_2CO_2H)(CH_2CO_2)_2)_3]\cdot 9H_2O$

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Much attention has been paid to the incomplete cubane-type Mo(IV) aqua ion with an oxygen bridge, $Mo_3O_4^{4+}$ [1]. Recently, a series of aqua ion† with sulphur bridge(s), $Mo_3O_{4-n}S_n^{4+}$ ($n = 1-4$), have been obtained and characterized [2–12], and the core structures have been elucidated by X-ray structure analyses of compounds derived from them. Corresponding tungsten(IV) aqua ions, $W_3O_{4-n}S_n^{4+}$ ($n = 0, 2, 3, 4$), have also been prepared and characterized [13–17]. However, the aqua ion, $W_3O_3S^{4+}$, has not yet been characterized, though the preparation and structure of $[W_3O_3S(NCS)_9]^{5-}$ having a sulfur-capped W_3O_3S core have been reported [18].

A new triangular tungsten(IV) aqua ion, $W_3O_3S^{4+}$ (1), has been prepared by the reaction of $(NH_4)_2WS_4$ [19] with $K_3[W_2Cl_9]$ [20] in 3 M HCl. After the reaction mixture was heated, Sephadex G-15 column chromatography (1 M HCl) was applied to the solution. The orange–red solution ($\lambda_{max} = 465$ nm in 2 M HCl) was purified by use of a Dowex 50W-X4 cation exchanger (2 M HPTS: *p*-toluenesulfonic acid). The aqua ion is stable towards air oxidation. A derivative complex, $K_2[W_3O_3S(Hnta)_3]\cdot 9H_2O$ (2) was prepared from the aqua ion (H_3nta; nitrilotriacetic acid). *Anal.* Found (Calc.): K, 5.21 (5.43); N, 2.86 (2.91); C, 14.80 (15.02); H, 1.88 (2.73)%. Thiocyanato complex $[W_3O_3S(NCS)_9]^{5-}$ can also be easily prepared by the reaction of 1 with SCN^{1-}.

X-ray crystal structure analysis# of 2 revealed the existence of a sulfur-capped trinuclear tungsten core, $W_3(\mu_2\text{-}O)_3(\mu_3\text{-}S)$. A perspective view of the complex anion is shown in Fig. 1 together with the selected bond distances, the symmetry of C_3 being imposed. The core dimensions are not so different from those of $[W_3O_3S(NCS)_9]^{5-}$ (W–W, 2.612(6); W–S, 2.34(2); W–O, 1.98(2) Å) [18] and from those of the corresponding molybdenum complex, $[Mo_3O_3S(Hnta)_3]^{2-}$ (Mo–Mo, 2.589(6); Mo–S, 2.360(7); Mo–O, 1.917(9) Å) [2].

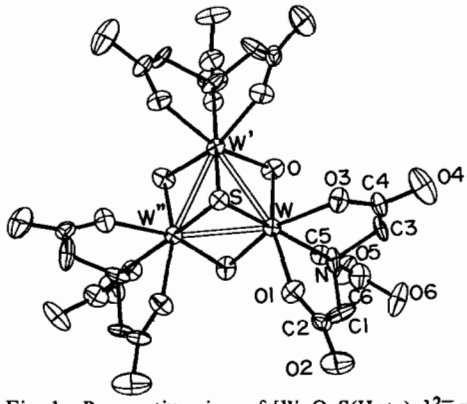

Fig. 1. Perspective view of $[W_3O_3S(Hnta)_3]^{2-}$ with selected bond distances (Å): W–W', 2.596(2); W–S, 2.380(8); W–O, 1.947(16); W'–O, 1.951(16); W–O1, 2.073(17); W–O3, 2.118(17); W–N, 2.236(20).

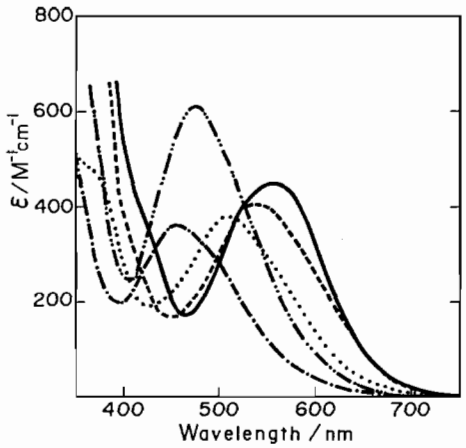

Fig. 2. Electronic spectra of tungsten(IV) aqua ions, $W_3O_{4-n}S_n^{4+}$ ($n = 1-4$), in 2 M HPTS and $[W_3O_3S(Hnta)_3]^{2-}$ in water. – · –, $W_3O_3S^{4+}$; ·····, $W_3O_2S_2^{4+}$; – – –, $W_3OS_3^{4+}$; ——, $W_3S_4^{4+}$; – ·· –, $[W_3O_3S(Hnta)_3]^{2-}$.

Electronic spectra of tungsten(IV) aqua ions, $W_3O_{4-n}S_n^{4+}$ ($n = 1, 2, 3, 4$) and 2 are shown in Fig. 2. Peak positions of the absorption spectra of tungsten aqua ions are listed in Table I together with those of the corresponding molybdenum aqua ions**.

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

#Crystal data: hexagonal system, space group $R\bar{3}$, $a = 17.347(9)$, $c = 23.532(5)$ Å, $V = 6130(5)$ Å^3, $Z = 6$, $D_m = 2.35$, $D_c = 2.34$ g cm^{-3}. Intensity data were collected on an automated four-circle diffractometer by use of graphite-monochromated Mo Kα radiation on the $2\theta \leq 50°$ range. The coordinate of W was determined by means of MULTAN, and the remaining non-hydrogen atoms were located from difference maps. The current R value is 0.058 for 1622 reflections ($F_o \geq 6\sigma(F_o)$).

**Table I includes the only clusters whose core structures have been determined by X-ray structure analyses; *cf.* ref. 8.

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TABLE I. Absorption Maxima[a] and ϵ Values[b] of Aqua Ions, $M_3O_{4-n}S_n^{4+}$ (M = Mo or W; n = 0–4), in HPTS in the Visible Region[c]

		M_3O_4	M_3O_3S	$M_3O_2S_2$	M_3OS_3	M_3S_4
M = Mo	λ_{max}	505	512	572	588	602
	ϵ	189	153	202	263	351
	Reference	1a	2	3	4	5
M = W	λ_{max}	455	457	506	535	557
	ϵ	375	361	380	407	446
	Reference	13b	this work	14	15	16[d]

[a]nm. [b]M^{-1} cm^{-1} per trimer. [c]All the sulphur-bridging clusters have μ_3-S. [d]Peak positions and ϵ values have been revised.

Substitution of μ_3-S for μ_3-O induces little change in the peak positions for both series, while the introduction of μ_2-S produces a rather large red shift.

Supplementary Material

Tables of atomic coordinates, thermal parameters, and bond distances and angles are available from the author (T.S.) on request.

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