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The Structure of $[W_3S_4(H_2O)_9](CH_3{\cdot}C_6H_4{\cdot}SO_3)_4{\cdot}7H_2O$. The First Example of X-ray Crystal Structure Analysis of Metal-cluster Aqua Ion

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Many metal-cluster compounds have been prepared and characterized [1]. The technique of X-ray crystal structure analysis has been used in most cases to determine the structure of clusters, though the analysis of EXAFS is also valid for some species in solution [2]. Since no crystals of cluster complexes with aqua ligands only have been obtained so far**, crystals of complex compounds obtained by the substitution of other ligands for aqua ligands have been employed for X-ray crystal structure analysis to know the structure of cluster aqua ions, assuming that the core structure of the cluster aqua ion is retained intact on the substitution reaction. The ^{18}O labelling experiment together with the X-ray structure analysis of the $[Mo_3O_4(NCS)_8H_2O)^{4-}$ complex ion by Murmann and Shelton [4] is the one and only case to give conclusive evidence for the retention of the Mo_3O_4 core of the $[Mo_3O_4(H_2O)_9]^{4+}$ aqua ion.

We report here the first example of preparation and X-ray crystal structure analysis of a metal-cluster compound, $[W_3S_4(H_2O)_9]{\cdot}(CH_3{\cdot}C_6H_4{\cdot}SO_3)_4{\cdot}7H_2O$ (**1**), which provides direct evidence of the $[W_3S_4(H_2O)_9]^{4+}$ aqua ion.

The aqua ion, $W_3S_4^{4+}$ in 2 M HCl, has been obtained by the reduction of $(NH_4)_2WS_4$ with $NaBH_4$ and purified by the use of Sephadex G-15 and Dowex 50W-X4 cation exchangers in succession†. Absorption of the solution to the Dowex 50W-X2 cation exchanger, slow elution with 4 M Hpts (*p*-toluenesulphonic acid), and then cooling of the eluted solution make **1** be deposited§.

A crystal of **1** suitable for X-ray measurement was sealed with epoxy resin to prevent dehydration. Crystal data: triclinic system, space group $P\bar{1}$, $a = 15.494(5)$, $b = 15.755(6)$, $c = 11.833(5)$ Å, $\alpha = 100.62(4)$, $\beta = 107.75(3)$, $\gamma = 76.08(3)$, $V = 2650.8(18)$ Å^3, $Z = 2$. Intensity data were collected on an automated four-circle diffractometer by the use of graphite-monochromated Mo Kα radiation on the $2\theta \leqslant 50°$ range. The coordinates of Mo and S atoms in the cation were determined by means of MULTAN, and the remaining non-hydrogen atoms were located from difference maps. The current R value is 0.0569 for 7107 reflections ($F_o > 5\sigma(F_o)$). The X-ray structure analysis shows clearly the existence of the W_3-triangular aqua ion, $[W_3S_4(H_2O)_9]^{4+}$ (Fig. 1). The W--W distance (average 2.724 Å) is slightly shorter than that (average 2.765 Å) in $[W_3S_4(NCS)_9]^{5-}$ [5], while the distances, W--μ_3–S and W--μ–S, are not so different from each other in both of the complexes.

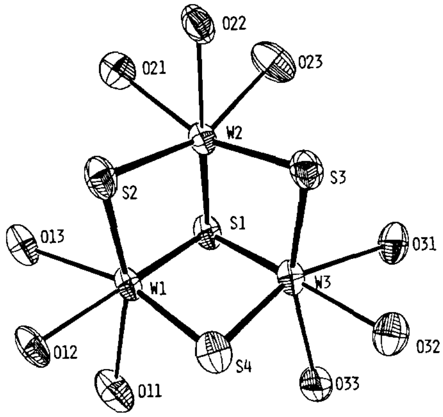

Fig. 1. Perspective view of $[W_3S_4(H_2O)_9]^{4+}$ with selected bond distances (Å): W1–W2, 2.721(2); W1–W3, 2.709(2); W2–W3, 2.742(2); W1–S1, 2.350(6); W2–S1, 2.336(4); W3–S1, 2.349(5); W1–S2, 2.287(5); W1–S4, 2.287(6); W2–S2, 2.279(6); W2–S3, 2.286(5); W3–S3, 2.291(5); W3–S4, 2.266(7); W–OH_2(av.), 2.187(13).

The cation, $[W_3S_4(H_2O)_9]^{4+}$, is surrounded by pts^- anions, every aqua ligand being connected to one of the oxygens of the pts^- anion through a hydrogen bond.

This technique of using concentrated Hpts solution to obtain crystals of the aqua ion is likely to be effective especially for sulphur rich aqua ions* and will give a direct evidence of the existence of metal-cluster aqua ions.

Supplementary Material

A list of atomic coordinates, thermal parameters, bond distances and angles can be obtained from author T.S. on request.

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**Some reports on mono nuclear aqua complexes have appeared; see for example ref. 3.

†Recently we reported the X-ray structure of $(bpyH)_5[W_3S_4(NCS)_9]{\cdot}3H_2O$, proposing the existence of the aqua ion, $[W_3S_4(H_2O)_9]^{4+}$ [5].

§*Anal.* Found (calc.): C, 19.82 (20.35); H, 3.74 (3.63)%.

*The X-ray structure analysis of $[Mo_3S_4(H_2O)_9](CH_3{\cdot}C_6H_4{\cdot}SO_3)_4{\cdot}nH_2O$ is in progress; see ref. 6.

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