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New Synthetic Route to $W_3S_4^{4+}$ Clusters: Preparation and Structure of $[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(S_4)_3(H_2O)_3]^{2-}$

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In recent years there has been increased interest in the trinuclear cluster thiocomplexes $M_3S_4^{4+}$ (M = Mo, W) having the structure of an incompleted cubane $[M_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]^{4+}$. Various synthetic procedures have been developed and complexes of $Mo_3S_4^{4+}$ with a wide range of ligands, such as CN^-, NCS^-, EDTA, NTA, IDA, [9]aneN_3 and phosphines, have been isolated and their structures characterized [1]. In addition, the whole series from $Mo_3S_4^{4+}$ to $Mo_3O_4^{4+}$ has been obtained [2]. Progress in the $W_3S_4^{4+}$ chemistry is less advanced. This is due to the lack of convenient methods for the synthesis of the starting $W_3S_4^{4+}$. The method of Shibahara *et al.* [3] involving treatment of $(NH_4)_2WS_4$ with $NaBH_4$ in a hydrochloric acid medium gives a 17% yield of the product. From this solution the $(bipyH)_5W_3S_4(NCS)_9\cdot3H_2O$ complex has been isolated and structurally characterized [3]. In 1988 Cotton and Llusar obtained $[W_3S_4(dmpe)_3Cl_3]PF_6\cdot H_2O$ crystals in a 20% yield by the interaction of WCl_4 with NaSH and subsequent treatment with dmpe and NH_4PF_6 [4].

In the present work we describe a new synthetic route to $W_3S_4^{4+}$ clusters starting from metallic tungsten.

Experimental

Tungsten (0.56 g), sulfur (0.20 g) and bromine (0.08 ml) were heated under conditions analogous to those described in ref. 5. The resulting brown compound was treated with 50 ml of an aqueous solution of $(NH_4)_2S_x$ ($x \approx 2$) at room temperature for 7 days. The black precipitate was washed with a small quantity of water and then with alcohol and boiling benzene; yield 0.85 g.

This product (0.25 g) was treated with 5 ml of boiling concentrated HCl and chromatographed on a DOWEX-50WX2. The violet band was eluted with 2M HCl. The W:S ratio in the obtained solution was 3:3.97 ± 0.03; the electronic spectrum (2 M HCl, $\lambda(\epsilon)$): 320 (8660); 570 (550) nm. The $W_3S_4^{4+}$ yield in solution (based on the starting metallic tungsten) was more than 50%.

The X-ray diffraction study was performed on single crystals from the reaction mixture. Using a Hilger–Watts Y290 diffractometer the intensities of 1174 reflections were measured at 20 °C (λ(Mo Kα), $2\theta = 60°$), trigonal crystals, $a = 12.508(1)$, $c = 10.112(1)$ Å, space group $P\bar{3}1c$, $Z = 2$. The structure has been solved by direct method and refined to $R = 0.043$ using 1073 reflections ($I \geqslant 3\sigma$) with corrections for absorption.

Results and Discussion

The structure of the cluster anion and the bond lengths are shown in Fig. 1. The $[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(S_4)_3(H_2O)_3]^{2-}$ cluster anion is in a special position on the three-fold axis passing through the μ_3-sulfide ligand S(6) and the centre of the W_3 triangle. The μ_2-bridging sulfur atoms occupy the side of the W_3 triangle opposite to μ_3-S(6); the valence angles W–μ_2-S–W are 75.11°.

Each tungsten atom in the cluster fragment $W_3S_4^{4+}$ is coordinated by a bidentate ligand S_4^{2-} and an oxygen atom of the water molecules. Without considering the metal–metal bonds, each W atom has a distorted octahedral coordination environment WS_5O with a *fac*-arrangement of the μ_n-S ligands.

A characteristic feature of the S_4^{2-} ligand is a slight alteration of the S–S bond lengths. The distance between the central S atoms in this ligand is 2.041 Å while the bonds to the peripheral S atoms are lengthened to 2.074 Å (av.). This redistribution of the S–S bond lengths is probably due to the different contributions from the π-interaction, a feature that is partially retained in the nonplanar metallocycles (which in $[W_3S_{16}(H_2O)_3]^{2-}$ have the configuration of a half-chair) [6]. It should be noted that the W–S bonds of the WS_5 cycle show a still more pronounced non-equivalence for the transoidal (2.467 Å) and cisoidal (2.539 Å) positions to the μ_3-S(6).

The powder diffraction pattern of the black crystalline substance prepared by the method described in the experimental part contains all of the reflections calculated from the data for the selected single crystals and only the most strong reflections of metallic tungsten. Procedures for purification of

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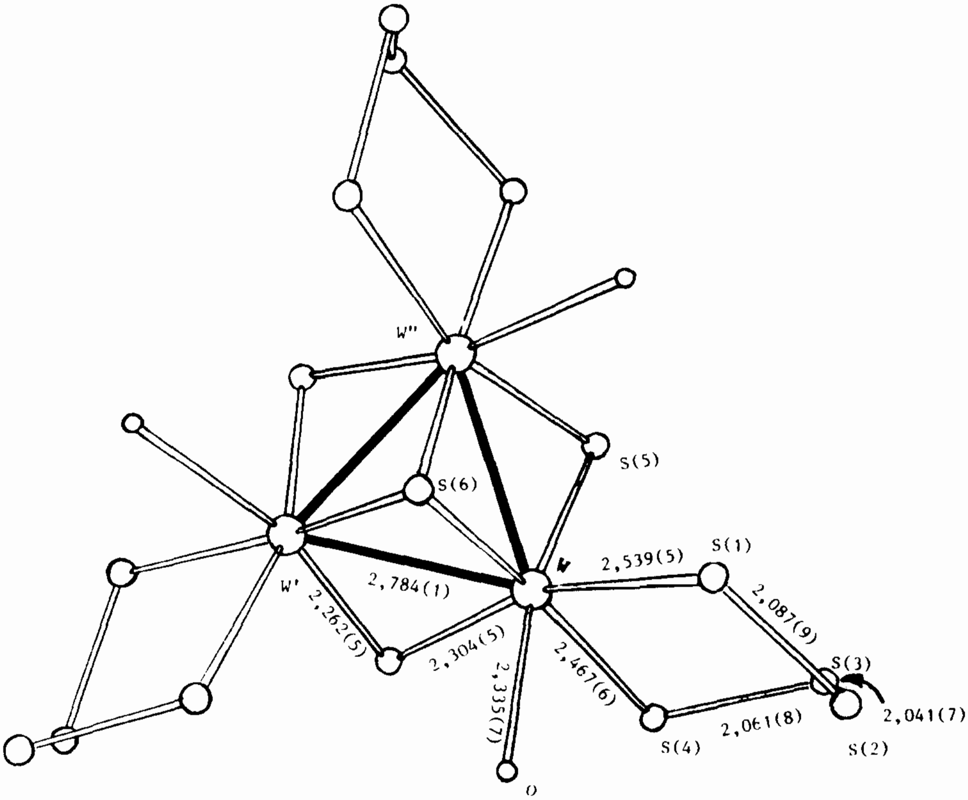

Fig. 1. The structure of $W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(S_4)_3(H_2O)_3{}^{2-}$.

the complex have not been found and therefore no correct analytical data could be obtained for the solid phase which complicated determination of the composition of the cation in the complex. Charge assignment to the anion complex $[W_3S_{16}(H_2O)_3]^{2-}$ has been made on the basis of its diamagnetism. According to the X-ray diffraction analysis the composition of the studied compound can be tentatively described as $[(NH_4)_3(HSO_3)][W_3S_{16}(H_2O)_3]$. The structure of the cationic aggregate which is present in the crystal along with the cluster is being refined.

Interaction with concentrated HCl and HBr acids leads to elimination of the $S_4{}^{2-}$ ligands, with the cluster fragment $W_3S_4{}^{4+}$ remaining intact and going into the solution. In 2 M HCl the electronic absorption spectrum coincides well with the spectrum for the solution in HPTS reported in ref. 3.

Because of their structure, the $M_3S_4{}^{4+}$ fragments are capable of coordinating an extra metal atom, completing the structure to a cubane. This offers new possibilities for the synthesis of heterometallic clusters. There are recent reports of complexes containing metal cluster cubane cations $Mo_3S_4M^{4+}$ (M = Fe, Co, Ni, Cu, Hg) [7–10]. For tungsten such compounds are not known. We found that the solution of $W_3S_4{}^{4+}$ in hydrochloric acid interacts, for example, with metallic copper. At present we are investigating heterometallic thiocomplexes W_3S_4-M^{n+}.

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