Crystal structure of bis(\(N,N,N\)-trimethylbutanaminium) tetrathiotungstate(VI), \((\text{BuMe}_3\text{N})_2[\text{WS}_4]\)

Abstract

C\(_{14}\)H\(_{36}\)N\(_2\)S\(_4\)W, monoclinic, \(C_2/c\) (no. 15), \(a = 16.175(3)\ \text{Å},\ b = 9.7755(15)\ \text{Å},\ c = 15.452(3)\ \text{Å},\ \beta = 115.183(7)^\circ,\ V = 2211.0(7)\ \text{Å}^3,\ Z = 4,\ R_{gt}(F) = 0.0190,\ wR_{ref}(F^2) = 0.0490,\ T = 223\ \text{K}.

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

\((\text{NH}_4)_2\text{WS}_4\) (0.030 g, 0.086 mmol) and \text{BuMe}_3\text{NI} (0.063 g, 0.26 mmol) were charged to a Pyrex tube with diameter of 9 mm and about 0.3 mL 1:2 (v/v) H\(_2\)O/MeOH mixture was added as a solvent. While the solvent was being frozen, the Pyrex tube was evacuated under vacuum and sealed with the use of a flame. The sealed tube was placed in an oven and heated at 90 °C for a day, then cooled to room temperature. Yellow orange polyhedral crystals were isolated by filtration and washed with MeOH and diethyl ether several times. Crystals of \((\text{BuMe}_3\text{N})_2[\text{WS}_4]\) were obtained in 13 % yield, based on the W metal used.

2 Experimental details

H atoms were positioned geometrically and treated as riding, with C–H = 0.98 (CH\(_2\)) and 0.97 (CH\(_3\)) Å with \(U_{	ext{iso}}(\text{H}) = 1.2\) (1.5 for methyl) \(U_{	ext{eq}}(\text{C})\). H atoms of the CH\(_2\) were positioned to be staggered with respect to the shortest other bond to the atom to which the CH\(_3\) is attached.

3 Comment

The title compound, \((\text{BuMe}_3\text{N})_2[\text{WS}_4]\), prepared by the solvothermal reaction of \((\text{NH}_4)_2\text{WS}_4\) and \text{BuMe}_3\text{NI} with a 1:2 (v/v)
H₂O/MeOH mixture as the solvent, is composed of a [WS₄]²⁻ molecular anion and two charge-balancing BuMe₃N⁺ cations. Soluble tetrathiotungstate compounds have focused much attention mainly due to their potential as precursors for the WS₂ HDS (HydroDeSulfurization) catalyst and the soft synthesis of WS₂ nanomaterials. The tetrathiotungstate [WS₄]²⁻ anion had been stabilized and structurally characterized with a number of cations such as NH₄⁺, Rb⁺, [Ni(tren)]⁺ there is minimal influence caused by the packing of unsymmetrical BuMe₃N⁺ cations and no strong interaction between the BuMe₃N⁺ cations and the [WS₄]²⁻ anions. Compared to the shortest S···H distance of 2.31 Å observed in ((CH₃)₂NH(CH₂)₂NH₃)[WS₄] (shortest S···H distance in this compound is significantly longer, measuring 2.8477(9) Å between S(1) and H(2B)), indicating a lack of H-bonding between the BuMe₃N⁺ cations and the [WS₄]²⁻ anions.

**Author contributions:** All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

**Competing interests:** The authors declare no conflicts of interest regarding this article.

**Research funding:** This work was supported by the Incheon National University Research Grant in 2020.

**References**


